

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

In re application of:
John L. Waddell Jr., et al
Application No. 10/630,897
Filed: July 31, 2003

ACOUSTIC SHOCK WAVE ATTENUATING ASSEMBLY

Examiner: Stephen Johnson
Art Unit: 3641

APPEAL BRIEF

Anne M. Kornbau
Registration No. 25,884
Attorney for Appellants

BROWDY AND NEIMARK, P.L.L.C.
1625 K Street, N.W.
Washington, D.C. 20006
Phone: 202-628-5197
Fax: 202-737-3528
Email: mail@browdyneimark.com

Attorney Docket: WADDELL 1

Date: January 28, 2011

TABLE OF CONTENTS

TABLE OF CONTENTS.....	i
TABLE OF AUTHORITIES.....	ii
REAL PARTY IN INTEREST	1
RELATED APPEALS AND INTERFERENCES.....	2
STATUS OF THE CLAIMS.....	3
STATUS OF AMENDMENTS	4
SUMMARY OF CLAIMED SUBJECT MATTER	5
GROUND OF REJECTION TO BE REVIEWED ON APPEAL.....	9
ARGUMENT	10
I. Claims 22 and 29 are not obvious over Bainbridge et al. in view of Takahashi.	10
II. Claims 13, 14, 17-19, 21 and 23-28 are not obvious over Bainbridge in view of Takahashi and further in view of Gettle et al., US 5,394,786.	15
CONCLUSION	18
CLAIMS APPENDIX.....	19
EVIDENCE APPENDIX	25
RELATED PROCEEDINGS APPENDIX.....	26

REAL PARTY IN INTEREST

The present appeal is taken from the final rejection mailed November 30, 2010.

The assignee of the subject application is BlastGard International, Inc., 2451 McMullen Booth Road, Suite 207, Clearwater, Florida 33759-1362.

TABLE OF AUTHORITIES

Cases

<i>Corning Glass Works v. Sumitomo Elec. U.S.A., Inc.</i> , 868 F.2d 1251, 9 USPQ2d 1962 (Fed. Cir. 1989)	13, 14
<i>Schering Corp. v. Gilbert</i> , 153 F.2d 428 (1946)	17
<i>Schriber-Schroth Co. v. Cleveland Trust Co.</i> , 311 U.S. 211 (1940)	16
<i>Seymour v. Osborne</i> , 11 Wall. 516, 547 (1861)	16

Statutes

35 U.S.C. 103(a)	9
------------------------	---

RELATED APPEALS AND INTERFERENCES

There are no related appeals and interferences.

STATUS OF THE CLAIMS

Claims 1-12, 15, 16 and 20 have been cancelled.

Claims 13, 14, 17-19 and 21-29 are rejected.

The rejection of claims 13, 14, 17-19 and 21-29 is appealed.

STATUS OF AMENDMENTS

The amendment filed October 8, 2010 has been entered.

SUMMARY OF CLAIMED SUBJECT MATTER

A flexible, shock-absorbing assembly is made of two flexible films such as polyamide, optionally waterproof, joined by seams which form pockets or cells. The pockets or cells contain shock-attenuating material selected from the group consisting of volcanic foam glasses, perlite, vermiculite and pumice (paragraphs [0016, 0039, 0043], claims 13, 14, 17-19 and 21). The flexible sheet is sufficiently porous with respect to acoustic or shock waves to allow the acoustic or shock waves to penetrate the film and contact the shock attenuating material (paragraph [0023]).

The assembly claimed provides a unique way of packaging a known shock attenuating material in such a form that the shock attenuating material can be made available to protect a variety of types of structure. The assembly is light and flexible and has been reputedly demonstrated to protect against the deleterious effects of shock waves resulting from explosions (paragraph [0021]).

The pockets may include, along with the shock attenuating material, at least one material selected from the group consisting of fireproofing materials, heat insulating materials, intumescent materials, and radiation insulating materials ([paragraphs [0019], claims 17, 18, 24, 25]).

The claimed invention additionally relates to a carrier for shock-attenuating material that is sufficiently flexible to wrap around a structure of any shape. This carrier includes a first and second films of flexible material that is

optionally water-impermeable. The first film and the second film are attached to each other by a plurality of seams that form spaced pockets, which pockets hold shock-attenuating material selected from the group consisting of volcanic foam glasses, perlite, vermiculite, and pumice. (paragraphs [0016, 0043], claims 23-29).

That is, the assembly claimed herein comprises:

(a) a first film of flexible resin material which is optionally water-impermeable or is optionally coated with water-impermeable material (paragraph [0016]);

(b) a second film of flexible resin material, wherein said second film of flexible resin is optionally water-impermeable or is coated with a water-impermeable material, wherein the second film of flexible resin material has attached pockets spaced from each other along the second film (paragraphs [0016] and [0027]);

(c) the first film is attached to the second film via a plurality of seams, wherein the seams surround each of the spaced pockets in such a manner as to make the assembly sufficiently flexible to surround a structure of any shape (paragraph [0016]);

(d) each of the pockets is filled with a flowable shock wave attenuating material selected from the group consisting of volcanic foam glasses, perlite, vermiculite, and pumice (paragraphs [0016], [0043]);

Support for this can be found in the specification as filed at paragraph [0016] on page 6, paragraph [0018] on page 7, paragraph [0021] on page 8 and paragraph [0023] on page 9.

Optionally, the pockets of the shock attenuating assembly can contain at least one of fireproofing materials, heat insulating materials, intumescent materials, and radiation insulating materials (paragraph [0019], page 7).

Claim 13 is drawn to a shock-attenuating assembly that is sufficiently flexible to wrap around any shaped structure (paragraph [0018], page 7) comprising, in combination,

(a) a first film of flexible resin material, wherein said first film of flexible resin material is optionally water-impermeable or is optionally coated with a water-impermeable material (paragraph [0020], page 8);

(b) a second film of flexible resin material, wherein said second film of flexible resin material is optionally water-impermeable or is optionally coated with a water-impermeable material, wherein said second film of flexible resin material has attached pockets spaced from each other along the second film (paragraph [0020], page 8);

(c) the first film attached to the second film via a plurality of seams, wherein the seams surround each of the spaced pockets in such a manner as to make the assembly sufficiently flexible to surround structure (paragraph [0016], page 6; paragraph [0018], page 7);

(d) each of the pockets filled with a shock wave attenuating material selected from the group consisting of perlite, vermiculite, pumice and foamed volcanic glass (paragraphs [0023-0027], pages 9 and 10). Also see Figure 1.

Claim 22 is drawn to a flexible shock-attenuating assembly comprising in combination:

(a) a first strip of a water-impermeable polyamide resin material (paragraph [0039], page 13);

(b) a second strip of a water-impermeable polyamide resin material, said second strip having attached pockets spaced from each other along the second strip (paragraph [0016], page 6);

the first strip attached to the second strip via a plurality of seams, the seams surrounding each of the spaced pockets in such a way as to make the assembly flexible (paragraph [0018], page 7).

Claim 23 is drawn to a carrier for shock-attenuating material a first strip of a water-impermeable polyamide resin material [paragraph 0039, page 13] a second strip of a water-impermeable polyamide resin material, said second strip having attached pockets spaced from each other along the second strip (paragraph [0016], page 6);

the first strip attached to the second strip via a plurality of seams, the seams surrounding each of the spaced pockets in such a way as to make the assembly flexible (paragraph [0018], page 7).

GROUND OF REJECTION TO BE REVIEWED ON APPEAL

Claims 22 and 29 are rejected under 35 U.S.C. 103(a) as being unpatentable over Bainbridge et al., US Patent No. 6,453,477 in view of Takahashi, US Patent No. 5,910,540.

Claims 13, 14, 17-19, 21 and 23-28 are rejected under 35 U.S.C. 103(a) as being unpatentable over Bainbridge in view of Takahashi as applied to claim 22 above, and further in view of Gettle et al., US Patent 5,394,786.

ARGUMENT

I. Claims 22 and 29 are not obvious over Bainbridge et al. in view of Takahashi.

The Examiner alleges that Bainbridge discloses a shock-attenuating assembly comprising: first and second plastic confinement layers made of water impermeable material including a plurality of pockets with stitching around the pockets, a shock wave attenuating material having the flow properties of a liquid, and fireproofing, heat insulating or intumescent material. Takahashi is cited for a disclosure of polyamide that forms a plastic layer.

It is respectfully submitted that the Examiner's characterization of Bainbridge is in error.

Bainbridge does not disclose a shock-attenuating assembly, but rather a protective padding for sports gear. The pad is filled with beads of elastic material. The beads are initially in compressed states within the casing. When a blow or force is applied, the beads are further compressed to absorb and dissipate the impact. Additionally, the applied blow or force will increase the tension in the outer casing to even further compress the elastic beads for better absorption and dissipation of the impact. In use, the porous pads are compressed and then they rebound to create a pumping effect that circulates air into and out of the pads, drawing heat and perspiration from the athlete's body (column 2, lines 48-62).

s discloses a porous, breathable pad (Abstract). The pads are overfilled and the casing are initially tensioned, so that the pads are biased toward a first shape and volume. That is, when the pads are unimpeded by any external forces, each pad will assume a first, predetermined shape such as the symmetrical one illustrated in Fig. 12. Depending upon the amount of overfill of the beads 22 and other factors such as the relative stiffness of the casing 20 and the relative spacing of any segments 34, the unrestrained single pouch 50 of the pad of FIG 12 tends toward a nearly circular cross section. (Column 6, lines 40-48). That is, the Bainbridge pad is a relatively inflexible pad.

In contrast thereto, the flexible assembly claimed herein is sufficiently flexible to wrap around any shaped structure,. It is clear from the description of the Bainbridge pad that the Bainbridge pad is not sufficiently flexible to be wrapped around a structure of any shape. Moreover, it is clear that the Bainbridge pad is designed for personal use to protect a body from impact and is not wrapped around any portion of the body, but lies flat against the part of the body protected.

Takahashi merely discloses that polyamide is a type of plastic. However, if the covering of the Bainbridge pad were polyamide, the pad itself would still not be sufficiently flexible to wrap around a structure of any shape.

The shock-attenuating assembly claimed herein is for attenuating shock waves from blasts resulting from explosive devices and the like. Explosive devices produce blast fragments emanating both from the device and from

material close to the point of explosion. Additionally, explosive devices produce shock waves, which produce the highly damaging phenomenon known as "blast." Pressure waves can be reflected and diffracted by phase boundaries, such as liquid droplets or solid particulates suspended in air. These deflections serve to increase the distance that the wave travels by a process of multiple reflections and diffractions. Scattering and dispersion thus produce more attenuation because they smear the discontinuity leading the shock wave, the result of which is a significant drop in pressure in the material. Shock waves are completely different from the impact against which the Bainbridge pad is to protect a body.

Explosions differ from a single impact situation, such as those from which the Bainbridge pad is designed to protect an individual, because explosions produce shock waves, which produce a highly damaging phenomenon known as blast. Rather than a single impact, shock waves are a plurality of pressure waves. One produced, shock waves propagate outwardly from the source of explosion. When shock waves pass into the shock attenuating material, turbulent zones are created, along with large numbers of miniature shock waves as energy from the shock wave passes into and through the flowable attenuating medium. The attenuating medium absorbs substantial energy from the shock waves, which is enhanced by confinement in the cells or recesses of the claimed assembly.

The mechanisms of the shock attenuating materials used in the herein claimed shock attenuating assembly are discussed in the specification at paragraphs 0045 through 0049. The shock-attenuating material I in the herein claimed assembly are solids with entrained gas, such as perlite, pumice, vermiculite and inorganic solid foams. These shock absorbing materials dramatically reduce the sound speed of the shock, as scattered, slowed, and reflected waves become coincident. The propagation paths of pressure waves through the shock absorbing material are substantially lengthened by their scattering and disposition.

It is clear from the specification that the presently claimed assembly is for blast or shock attenuation, not for any other purpose. The preamble of the claims, "A shock-attenuating assembly", defines the invention, which is further characterized by the fact that the assembly includes "a shock wave attenuating material selected from the group consisting of perlite, vermiculite, pumice and volcanic foam glasses". As the Federal Circuit stated in *Corning Glass Works v. Sumitomo Elec. U.S.A., Inc*, 868 F.2d 1251, 9 USPQ2d 1962 (Fed. Cir. 1989): "The determination of whether preamble recitations are structural limitations or mere statements of purpose or use can be resolved only on review of the entirety of the patent to gain an understanding of what the inventors actually invented and intended to encompass by the claim."

The present case is similar to the situation in *Corning, supra*, in that the defendant alleged that the claim was anticipated by a disclosure of a

substantially transparent luminescent glass in the form of a fiber comprised of a doped silica core having a sheath of silica. Although nothing in the cited patent discussed the use of the fiber as an optical waveguide, the defendant alleged that the fiber “inherently” could function as a waveguide. In *Corning*, the plaintiff defined the preamble words “an optical waveguide” in the specification. In *Corning*, it was clear from the specification that the inventors were working on the particular problem of an effective optical communication system, not on general improvements in conventional optical fibers. “To read the claim in light of the specification indiscriminately to cover all types of optical fibers would be divorced from reality. The invention is restricted to those fibers that work as waveguides as defined in the specification, which is not true with respect to fibers constructed with the limitations of paragraph (a) and (b) only. Thus, we conclude that the claim preamble in this instance does not merely state a purpose or intended use of the claimed structure... Rather, those words do give ‘life and meaning’ and provide further positive limitations to the invention claimed.”

In a similar manner, the present specification defines a shock-attenuating assembly as one providing shock wave, and therefore blast, attenuation capabilities in both confined spaces and unconfined areas, as described in paragraphs [0016] and [0020]. The problems in dealing with explosive devices are presented in great detail in the “Background” section of the present application, at paragraphs [0002] to [0005].

One of the advantages of the presently claimed assembly is that it is sufficiently flexible to be wrapped around a structure of any shape. In fact, the trash cans in the D.C. area METRO system are lined with BLASTWRAP®. The BLASTWRAP® is sufficiently flexible to line a cylindrical trash container.

The flexible shock absorbing assembly claimed herein provides a unique way of packaging a known shock attenuating material in such form that the shock attenuating material can be shaped to protect a variety of types of structure. The assembly is light and flexible and has been repeatedly demonstrated to protect against the deleterious effects of shock waves resulting from explosions.

The flexible assembly claimed herein uses a granular, crushable material that has energy absorbing properties. This material neither stiffens nor hardens when impacted by a shock wave, but is rapidly compressed and crushed to a fine powder, thus absorbing shock energy. The shock attenuating material used in the herein claimed assembly is designed not to resist shock force but to be consumed and destroyed by the force. The flexibility of the assembly allows it to be formed around structures of any shape.

II. Claims 13, 14, 17-19, 21 and 23-28 are not obvious over Bainbridge in view of Takahashi and further in view of Gettle et al., US 5,394,786.

In this rejection, the Examiner relies upon Bainbridge and Takahashi as cited against claims 22 and 29. However, it is clear from the above

that the flexible assembly claimed herein is entirely different from the relatively inflexible pad as disclosed by Bainbridge.

Gettle adds nothing to the combination of Bainbridge and Takahashi. Gettle merely discloses that perlite is a shock absorbing material. Putting perlite into the Bainbridge pad, which has a polyamide exterior, would still not lead to the presently claimed flexible assembly. The pad including perlite as a shock absorbing medium would still be a pad, and would not be sufficiently flexible to be wrapped around a structure of any shape. Moreover, perlite or foamed inorganic glasses would shatter upon impact, which is different from the material in the Bainbridge pad, which is compressed to absorb the impact.

The declaration of one of the inventors, James Gordon, was submitted with the amendment filed March 23, 2006, in order to demonstrate that the herein claimed invention satisfied a long-felt need for material that can be readily used to absorb the effects of a blast, and that can be readily conformed to any desired shape and size. The U.S. government has placed BlastGard, maker of BLASTWRAP®, the product covered by the present claims, as the sole source. BlastGard is the only U.S. company that offers a bomb resistant trash receptacle.

There is nothing in any of the patents cited above that even suggests that the assemblies disclosed therein can be used for blast protection. It is well settled law that claims are to be construed in light of the specification, and both are to be read with a view to ascertaining the invention, *Seymour v. Osborne*, 11 Wall. 516, 547 (1861); *Schriber-Schroth Co. v. Cleveland Trust Co.*, 311 U.S. 211

(1940); *Schering Corp. v. Gilbert*, 153 F.2d 428 (1946). It is clear from the specification and claims of the present application that applicants claim a shock-attenuating assembly that is designed to protect objects and environments from the effects of a blast or explosion. Trash receptacles in the D.C. area Metro system are lined with a flexible assembly as claimed herein.

The Examiner has cited no references that disclose the invention claimed herein, namely, a blast attenuating assembly sufficiently flexible to wrap around any shaped structure, comprising a first and second film of flexible material that are optionally water-impermeable or treated with a water-impermeable material, wherein the first film is attached to the second film by a plurality of seams forming pockets between the two films, and wherein each of the pockets is filled with a shock wave attenuating material selected from the group consisting of foamed volcanic glass, perlite, vermiculite and pumice.

CONCLUSION

For the reasons given above, it is respectfully submitted that the claims at bar are allowable over the cited art.

Applicant respectfully requests reversal of the Examiner's rejections.

Respectfully submitted,

BROWDY AND NEIMARK, P.L.L.C.
Attorneys for Applicant(s)

By: _____



Anne M. Kornbau
Registration No. 25,884

AMK:srd
Telephone No.: (202) 628-5197
Facsimile No.: (202) 737-3528
G:\BN\B\Blas\Waddell1\Pto\2011-01-28AppealBrief.doc

CLAIMS APPENDIX

This listing of claims includes all of the claims involved in the appeal.

Listing of Claims:

13. A shock-attenuating assembly that is sufficiently flexible to wrap around any shaped structure, said assembly comprising, in combination,
- (a) a first film of flexible resin material, wherein said first film of flexible resin material is optionally water-impermeable or is optionally coated with a water-impermeable material;
 - (b) a second film of flexible resin material, wherein said second film of flexible resin material is optionally water-impermeable or is optionally coated with a water-impermeable material, wherein said second film of flexible resin material has attached pockets spaced from each other along the second film;
 - (c) the first film is attached to the second film via a plurality of seams, wherein the seams surround each of the spaced pockets in such a manner as to make the assembly sufficiently flexible to surround a structure of any shape;

- (d) each of the pockets is filled with a flowable shock wave attenuating material selected from the group consisting of volcanic foam glasses, perlite, vermiculite and pumice; and
- (e) wherein both the first film and the second film are sufficiently porous with respect to acoustic or shock waves or gas to allow the acoustic or shock wave to penetrate the film to reach the flowable shock wave attenuating material.

14. The flexible shock-attenuating assembly according to claim 13 wherein the shock attenuating material is perlite.

17. The flexible shock-attenuating assembly according to claim 13 further including within the pockets at least one material selected from the group consisting of fireproofing materials, heat insulating materials, intumescent materials, and radiating insulating materials.

18. The flexible shock-attenuating assembly according to claim 13 further including within the pockets a fire retarding material.

19. The flexible shock-attenuating assembly according to claim 13 wherein the assembly is adapted and constructed so that the assembly can be cut along the seams so that shock attenuating material remains confined in the pockets.

21. The flexible shock-attenuating assembly according to claim 13 wherein the flexible sheets are water-impermeable.

22. A flexible shock-attenuating assembly comprising in combination:

- (a) a first strip of a water-impermeable polyamide resin material;
- (b) a second strip of a water-impermeable polyamide resin material, said second strip having attached pockets spaced from each other along the second strip;
- (c) the first strip attached to the second strip via a plurality of seams, the seams surrounding each of the spaced pockets in such a way as to make the assembly flexible; and

wherein both the first strip and the second strip are sufficiently porous with respect to acoustic or shock waves to allow the acoustic or shock wave to penetrate the strip to reach shock wave attenuating material contained in the pockets.

23. A carrier for shock-attenuating material, which carrier is sufficiently flexible to wrap around a structure of any shape structure, said carrier and shock attenuating material comprising, in combination,

- (a) a first film of flexible resin material, wherein said first film of flexible resin material is optionally water-impermeable or is optionally coated with a water-impermeable material;

- (b) a second film of flexible resin material, wherein said second film of flexible resin material is optionally water-impermeable or is optionally coated with a water-impermeable material, wherein said second film of flexible resin material has attached pockets spaced from each other along the second film;
- (c) the first film is attached to the second film via a plurality of seams, wherein the seams surround each of the spaced pockets in such a manner as to make the carrier sufficiently flexible to surround any shaped structure;
- (d) each of the pockets is filled with a shock wave attenuating material selected from the group consisting of volcanic foam glasses, perlite, vermiculite, and pumice; and
- (e) wherein both the first film and the second film are sufficiently porous with respect to acoustic or shock waves to allow the acoustic or shock wave to penetrate the film to reach the flowable shock wave attenuating material.

24. The carrier according to claim 23 wherein the shock wave attenuating material is perlite.

25. The carrier according to claim 23 further including within the pockets at least one material selected from the group consisting of fireproofing materials, heat insulating materials, intumescent materials, and radiating insulating materials.

26. The carrier according to claim 23 further including within the pockets a fire retarding material.

27. The carrier according to claim 23 wherein the carrier is adapted and constructed so that the carrier can be cut along the seams so that shock attenuating material remains confined in the pockets.

28. The carrier according to claim 23 wherein the flexible sheets are water-impermeable.

29. A carrier for flowable shock-wave attenuating material comprising in combination:

- (a) a first strip of a water-impermeable polyamide resin material;
- (b) a second strip of a water-impermeable polyamide resin material, said second strip having attached pockets spaced from each other along the second strip;
- (c) the first strip attached to the second strip via a plurality of seams, the seams surrounding each of the spaced pockets in such a way as to make the carrier flexible; and

wherein both the first strip and the second strip are sufficiently porous with respect to acoustic or shock waves to allow the acoustic or shock wave to penetrate the strip to reach shock wave attenuating material contained in the pockets.

EVIDENCE APPENDIX

Bainbridge et al., U.S. Patent No. 6,453,477;

Gettle et al., U.S. Patent 5,394,786; and

Takahashi, U.S. Patent No. 5,910,540.

RELATED PROCEEDINGS APPENDIX

There are no related proceedings in connection with the subject application.



US006453477B1

(12) **United States Patent**
Bainbridge et al.

(10) Patent No.: **US 6,453,477 B1**
 (45) Date of Patent: **Sep. 24, 2002**

(54) **PROTECTIVE PADDING FOR SPORTS GEAR**

(75) Inventors: **David W. Bainbridge**, Golden; **L. Paul Nickerson**, Superior; **Grant C. Denton**, Boulder, all of CO (US)

(73) Assignee: **Brock USA, LLC**, Boulder, CO (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/091,323**

(22) Filed: **Mar. 4, 2002**

Related U.S. Application Data

(63) Continuation of application No. 09/506,507, filed on Feb. 17, 2000, now Pat. No. 6,357,054, which is a continuation-in-part of application No. 09/226,311, filed on Jan. 7, 1999, now Pat. No. 6,032,300, which is a continuation-in-part of application No. 09/158,088, filed on Sep. 22, 1998, now Pat. No. 5,920,915.

(51) Int. Cl.⁷ **A41D 13/00**

(52) U.S. Cl. **2/455; 2/267; 428/76**

(58) Field of Search **2/456, 455, 69, 2/16, 463, 464, 465, 467, 462, 410-411, 414, 68, 20, 22, 2.5, 102, 70, 92, 161.1, 909, 910, 911, 227, 267, 268, DIG. 1, DIG. 3; 5/655.4, 953, 911, 702; 128/878, 881, 882; 602/23, 25, 27, 62, 63, 65; 428/76, 313.5**

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,652,776 A 12/1927 Galanis
 2,179,631 A 11/1939 Holder
 2,298,218 A 10/1942 Madson
 2,404,758 A 7/1946 Teague et al.

3,006,780 A 10/1961 Shaffer
 3,304,219 A 2/1967 Nickerson
 3,354,578 A 11/1967 Ryan
 3,459,179 A 8/1969 Olesen
 3,477,562 A 11/1969 Allen et al.

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

CH 577 328 7/1976
 FR 2495-453 6/1982
 FR 2616-655 12/1988
 GB 1 378 494 12/1974

OTHER PUBLICATIONS

Sales Literature of Faytex Corp., circa 1998.
 Sales Literature of JSP International 1998.
 24 Page Brochure of Porex Technologies 1989-1992.
 Sales Literature of JSP International with Product Samples 1998 and larger sample of one of the materials.

Primary Examiner—Gloria M. Hale

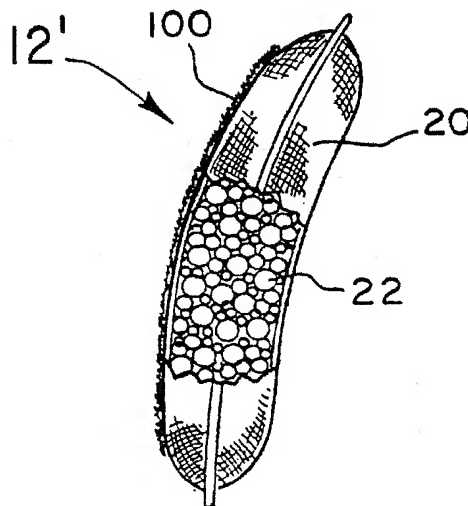
Assistant Examiner—Tejash Patel

(74) *Attorney, Agent, or Firm*—W. Scott Carson

(57) **ABSTRACT**

A porous, breathable pad for use as protective padding by a person to absorb the force of an impact and to protect the user from injury while allowing liquids and air to freely pass through the pad. The pad includes a plurality of discrete, solid beads of inelastic and waterproof, closed-cell foam wherein some outer portions of adjacent beads abut one another and other outer portions of the adjacent beads are spaced from each other to create interstitial spaces. In the preferred embodiments, substantially all of the adjacent beads are fused together at their abutting, outer portions and the interstitial spaces are substantially uniformly distributed throughout the pad.

4 Claims, 17 Drawing Sheets



US 6,453,477 B1

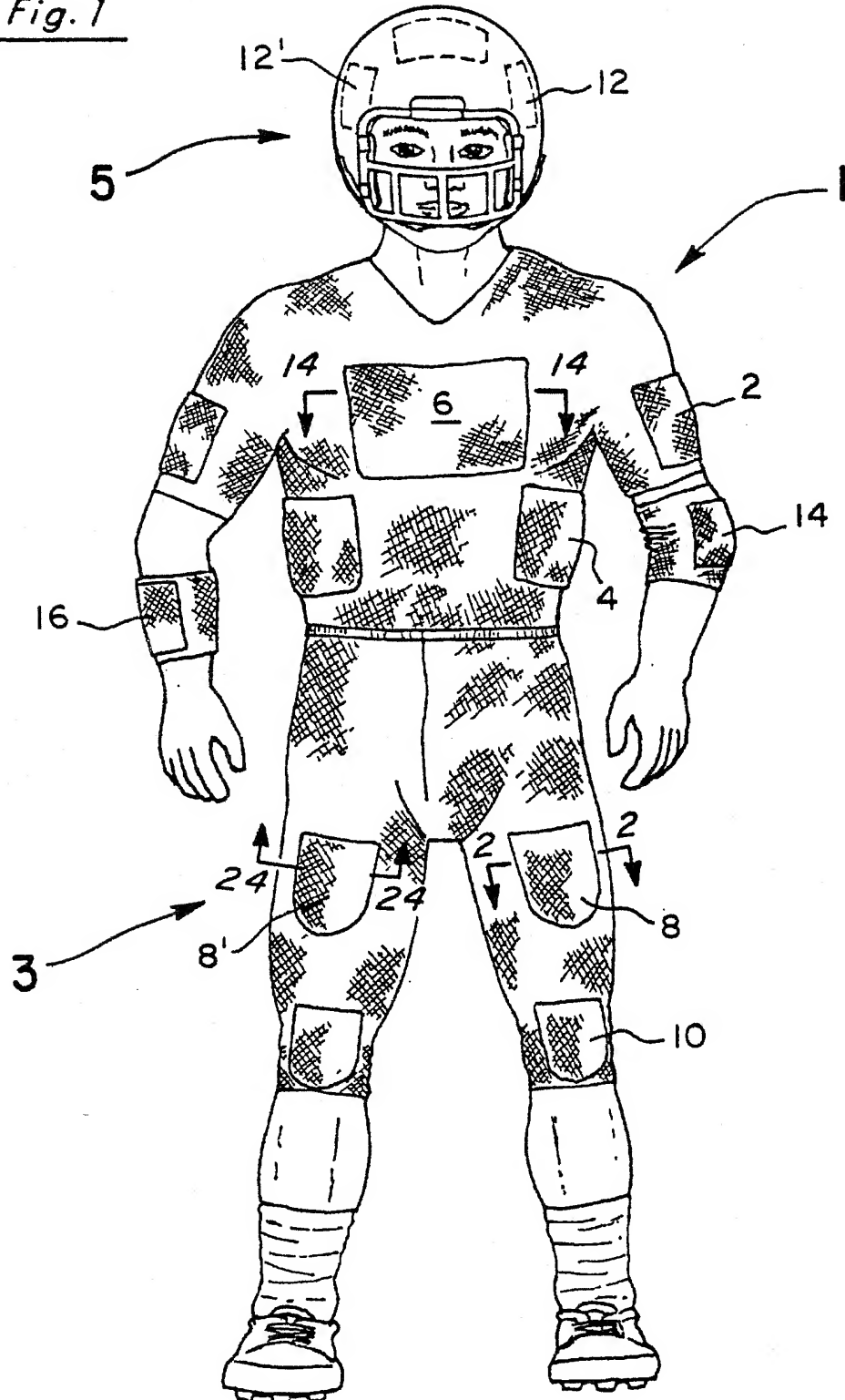
Page 2

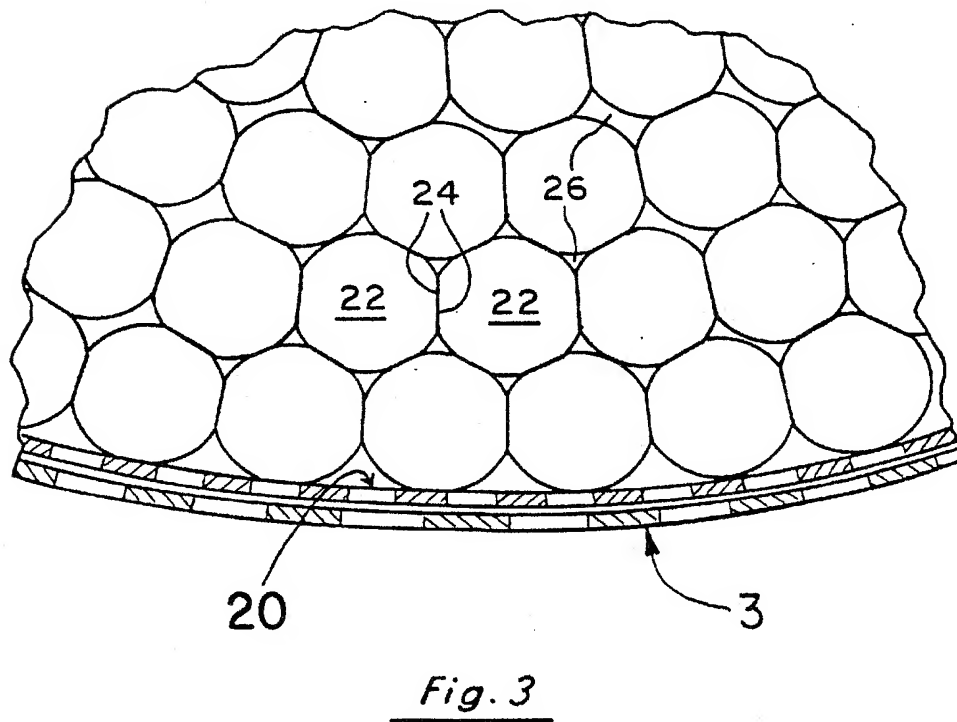
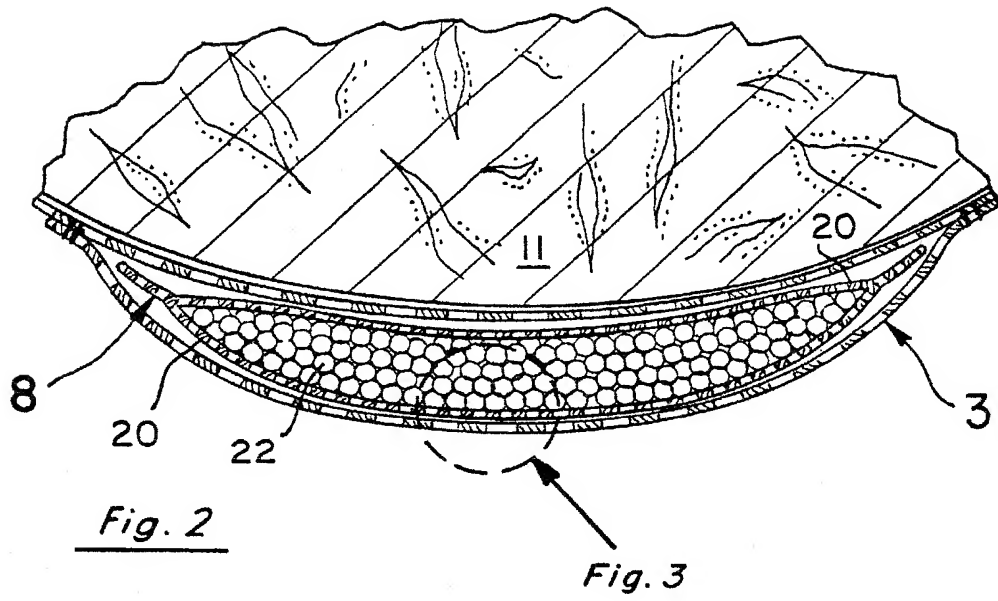
U.S. PATENT DOCUMENTS

3,489,154 A	1/1970	Kaspar et al.	4,740,416 A	4/1988	DeCoste, Jr. et al.
3,503,841 A	3/1970	Sterrett	4,751,202 A	6/1988	Toussaint
3,529,306 A	9/1970	Thorne	4,751,203 A	6/1988	Toussaint
3,552,044 A	1/1971	Wiele	4,756,026 A	7/1988	Pierce
3,563,837 A	2/1971	Smith et al.	4,855,170 A	8/1989	Darvell et al.
3,606,726 A	9/1971	Spertus et al.	4,905,320 A	3/1990	Squvers, Jr.
3,608,961 A	9/1971	Heck	4,989,794 A	2/1991	Askew et al.
3,616,162 A	10/1971	Noziere	5,052,874 A	10/1991	Johanson
3,629,882 A	12/1971	Thorne	5,055,340 A	10/1991	Matsumura et al.
3,640,787 A	2/1972	Heller	5,073,444 A	12/1991	Shanelee
3,663,344 A	5/1972	Brock et al.	5,079,787 A	1/1992	Pollmann
3,663,469 A	5/1972	Weissmahr	5,080,737 A	1/1992	Shoner
3,676,288 A	7/1972	Hoyle	5,103,517 A	4/1992	Krouskoo
3,755,063 A	8/1973	Massev et al.	5,134,725 A	8/1992	Yeshurun et al.
3,762,404 A	10/1973	Sakita	5,134,726 A	8/1992	Ross
3,816,234 A	6/1974	Winfield	5,152,019 A	10/1992	Hirata
3,857,731 A	12/1974	Merrill, Jr. et al.	5,201,780 A	4/1993	Dinsmoor, III et al.
3,864,181 A	2/1975	Wolinski et al.	5,279,237 A	1/1994	Alivizatos
3,889,444 A	6/1975	Davis et al.	5,292,840 A	3/1994	Heilmann et al.
3,968,530 A	7/1976	Dyson	5,301,370 A	4/1994	Henson
3,968,620 A	7/1976	Keltner	5,351,830 A	10/1994	Bender et al.
3,978,263 A	8/1976	Wellensiek	5,369,829 A	12/1994	Jay
4,011,611 A	3/1977	Lederman	5,397,620 A	3/1995	Hord, III
4,054,204 A	10/1977	Keeton	5,464,443 A	11/1995	Wilson et al.
4,102,109 A	7/1978	Modra et al.	5,515,975 A	5/1996	Jarvis et al.
4,121,399 A	10/1978	Verville	5,537,688 A	7/1996	Reynolds et al.
4,139,920 A	2/1979	Evans	5,545,128 A	8/1996	Hayes et al.
4,171,549 A	10/1979	Morrell et al.	5,584,072 A	12/1996	Kim et al.
4,193,499 A	3/1980	Lookholder	5,587,231 A	12/1996	Mereer et al.
4,229,398 A	10/1980	Harvey	5,614,310 A	3/1997	Delgado et al.
4,239,519 A	12/1980	Beall et al.	5,622,030 A	4/1997	Steed et al.
4,240,998 A	12/1980	Lichter et al.	5,626,657 A	5/1997	Pearce
4,243,617 A	1/1981	Burge	5,669,079 A	9/1997	Morgan
4,343,047 A	8/1982	Lazowski et al.	5,675,844 A	10/1997	Guvton et al.
4,370,754 A	2/1983	Donzis	5,694,747 A	12/1997	Tesch
4,391,561 A	7/1983	Smith et al.	5,699,561 A	12/1997	Broersma
4,432,110 A	2/1984	Sutton	5,711,029 A	1/1998	Visco et al.
4,441,905 A	4/1984	Malmendier et al.	5,711,215 A	1/1998	Sextl et al.
4,443,286 A	4/1984	Ikeda et al.	5,712,015 A	1/1998	Guillem
4,472,472 A	9/1984	Schultz	5,720,714 A	2/1998	Penrose
4,475,248 A	10/1984	L'Abbe et al.	5,733,012 A	3/1998	Jones
4,492,877 A	1/1985	Burnett	5,746,013 A	5/1998	Fay, Sr.
4,577,358 A	3/1986	Glass	5,778,470 A	7/1998	Haider
4,606,087 A	8/1986	Alivizatos	5,826,273 A	10/1998	Eckes
4,607,403 A	8/1986	Alivizatos	5,888,642 A	3/1999	Meteer et al.
4,620,633 A	11/1986	Lookholder	5,916,672 A	6/1999	Reeves
4,624,893 A	11/1986	Shibano et al.	5,920,915 A *	7/1999	Bainbridge et al. 2/16
4,640,080 A	2/1987	Wright	6,027,806 A	2/2000	Abe et al.
4,642,814 A	2/1987	Godfrev	6,032,300 A *	3/2000	Bainbridge et al. 2/16
4,657,003 A	4/1987	Wirtz	6,055,676 A	5/2000	Bainbridge et al.
4,705,715 A	11/1987	DeCoste, Jr. et al.	6,357,054 B1 *	3/2002	Bainbridge et al. 2/267

* cited by examiner

Fig. 1





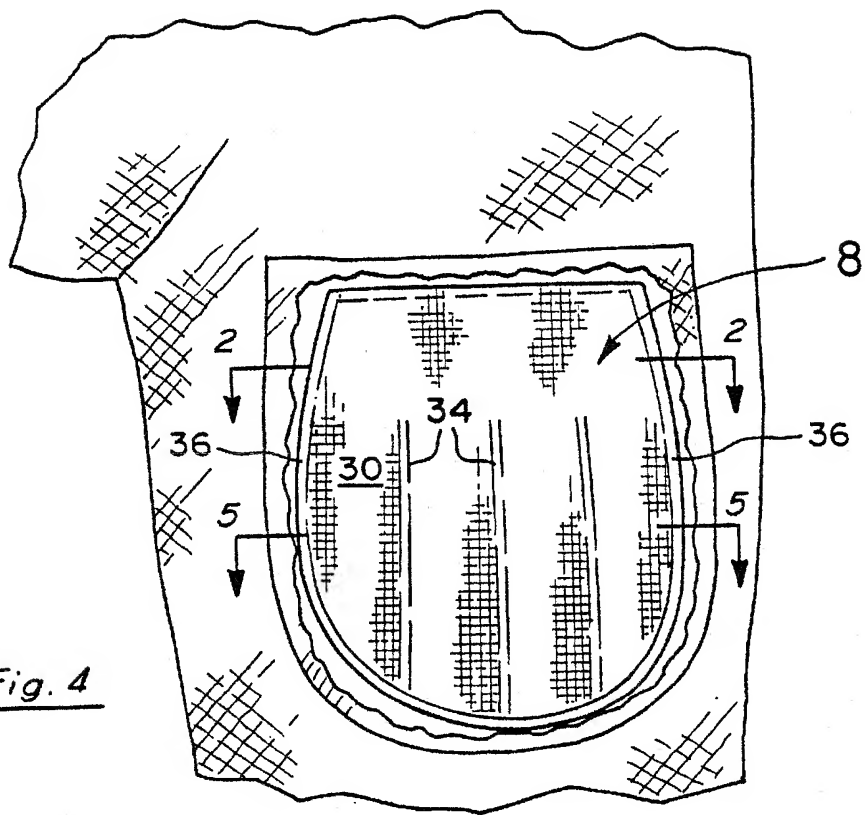
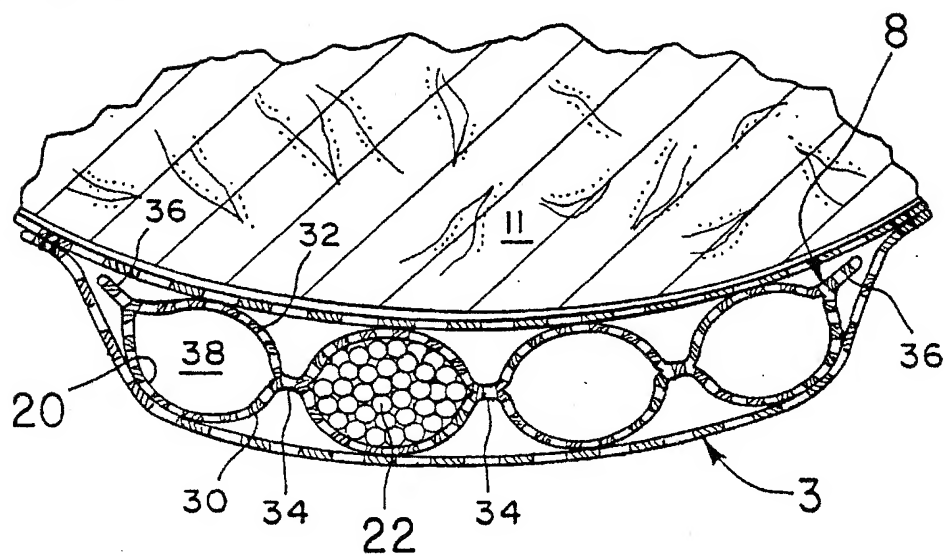


Fig. 5



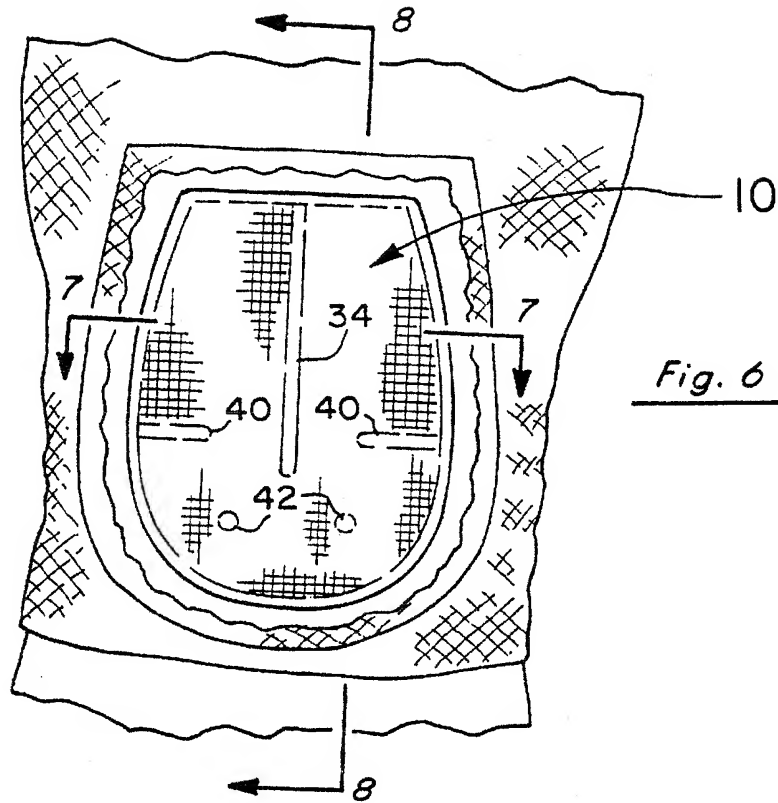


Fig. 6

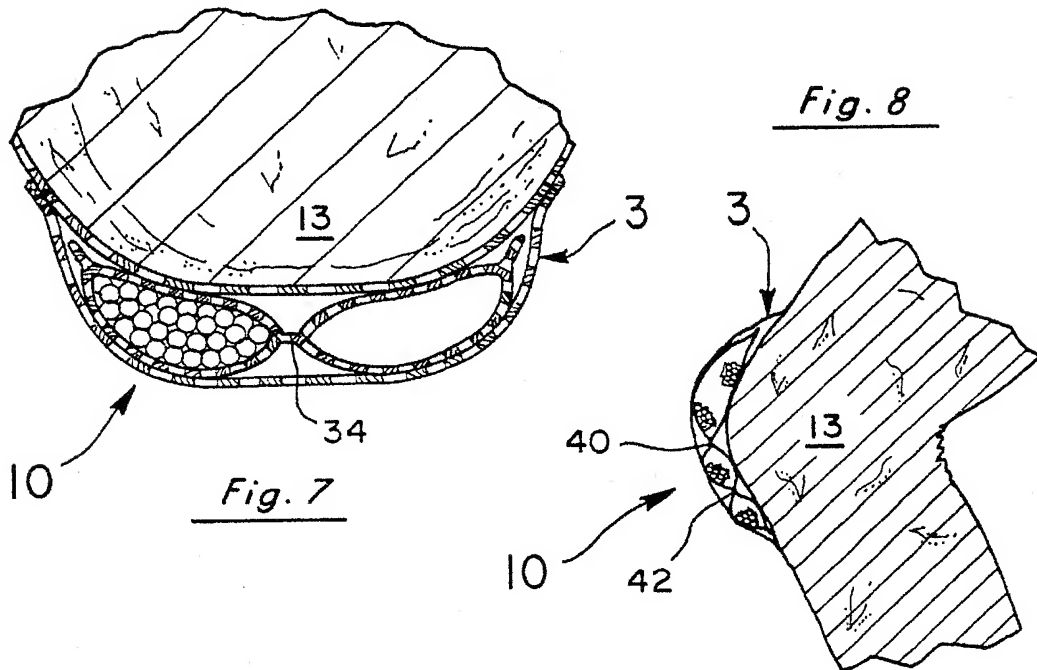


Fig. 8

Fig. 7

Fig. 9

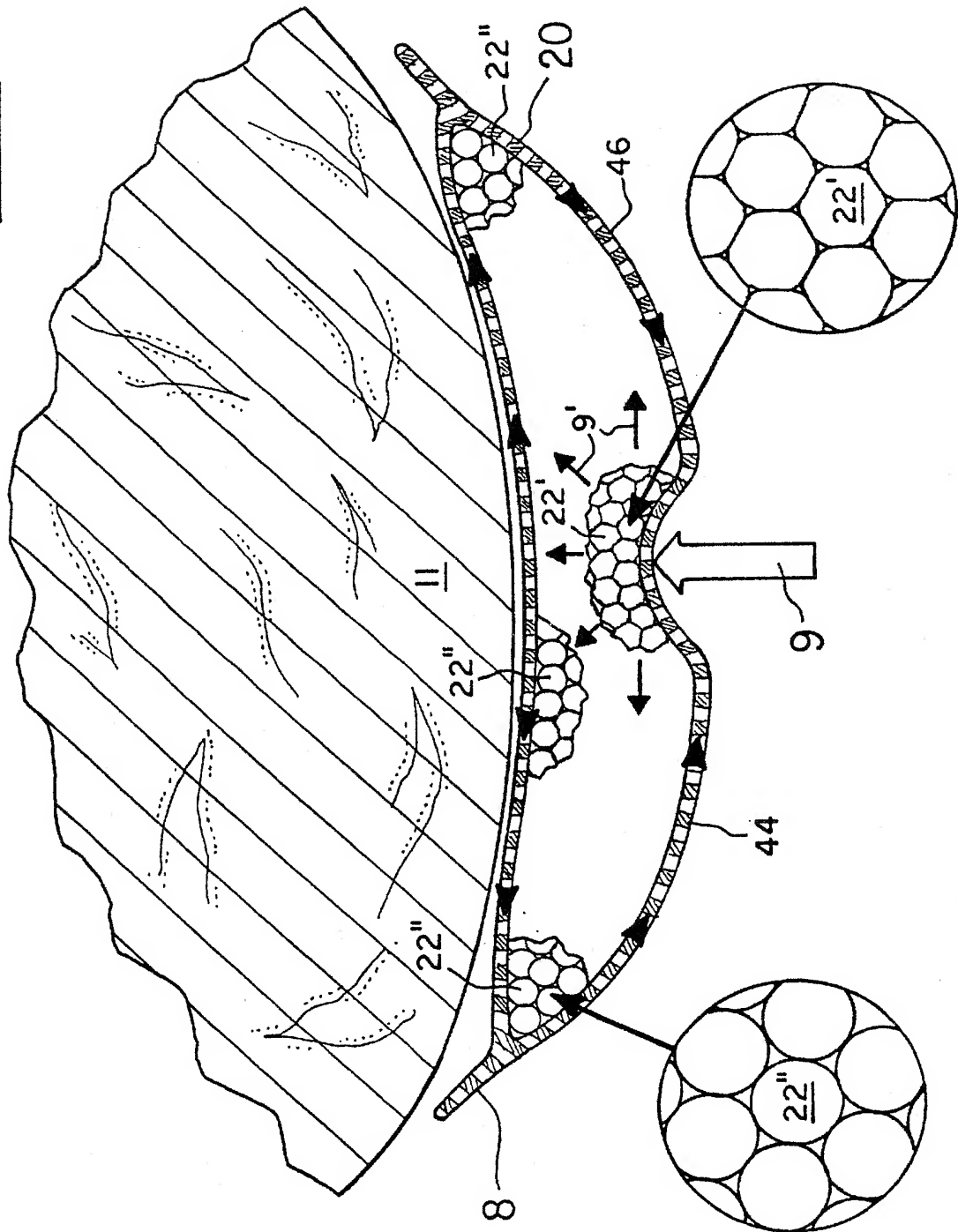


Fig. 10

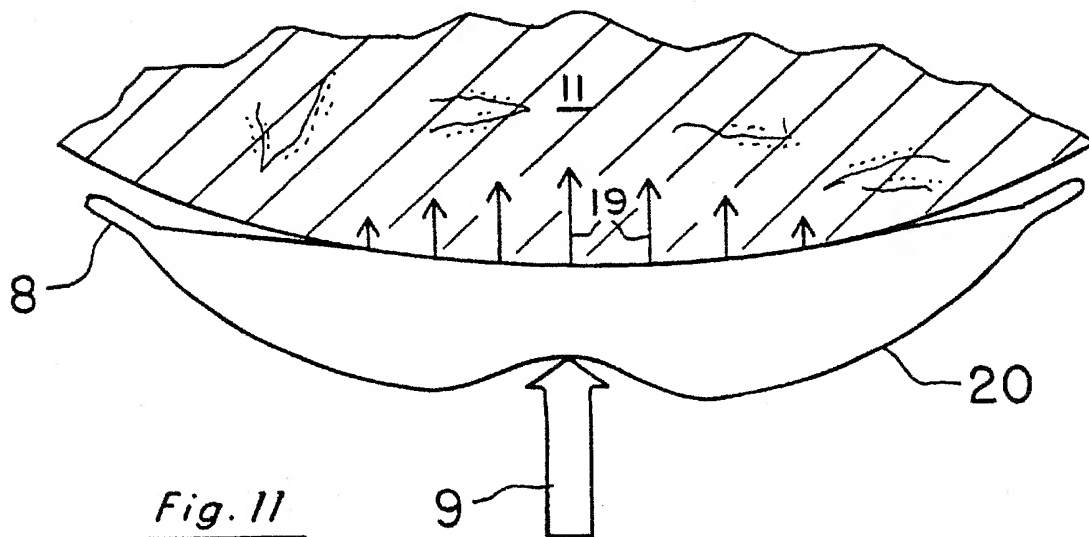
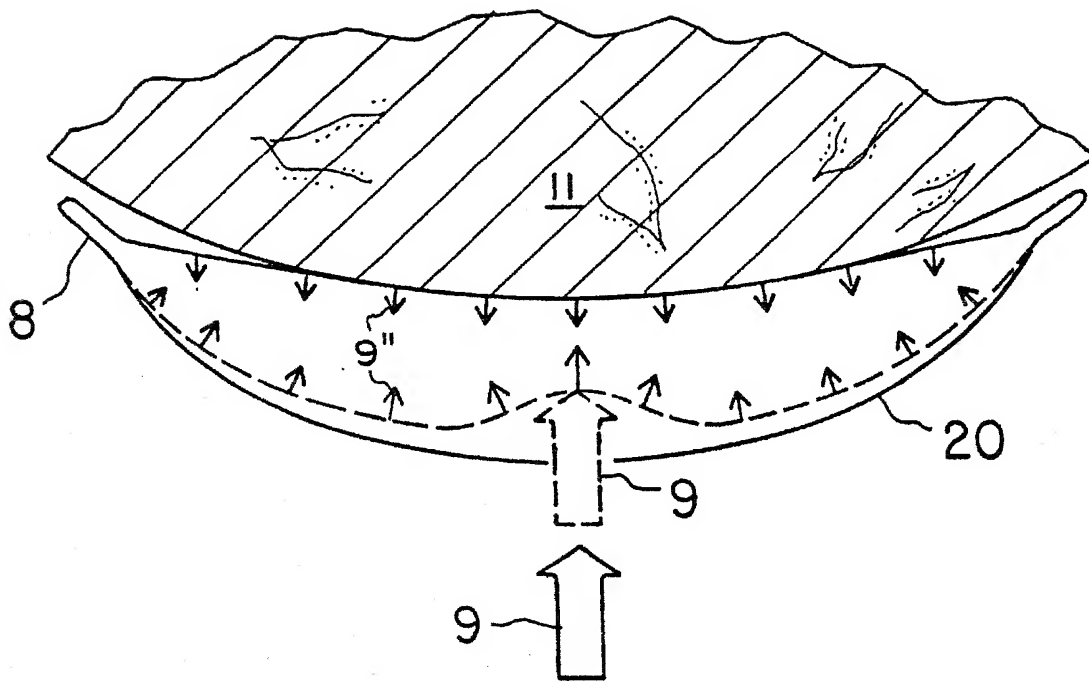


Fig. 12

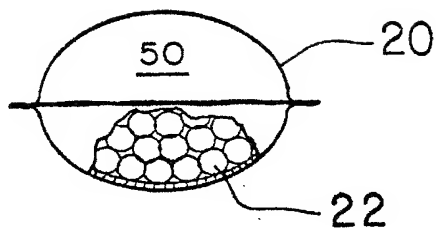


Fig. 13

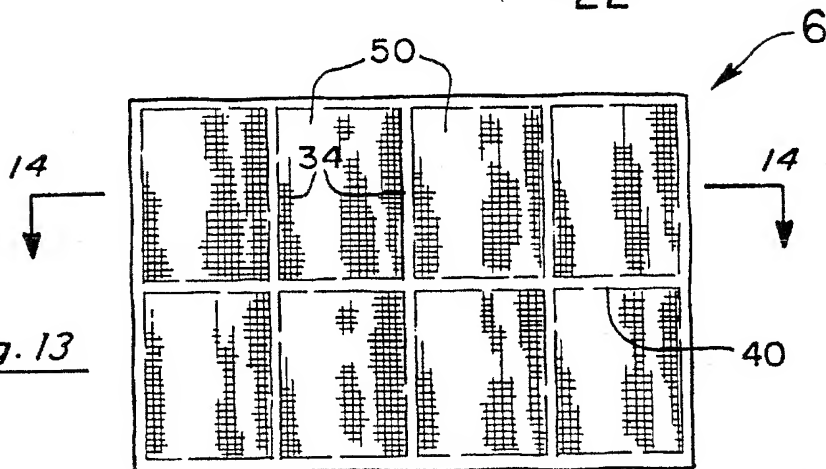


Fig. 14

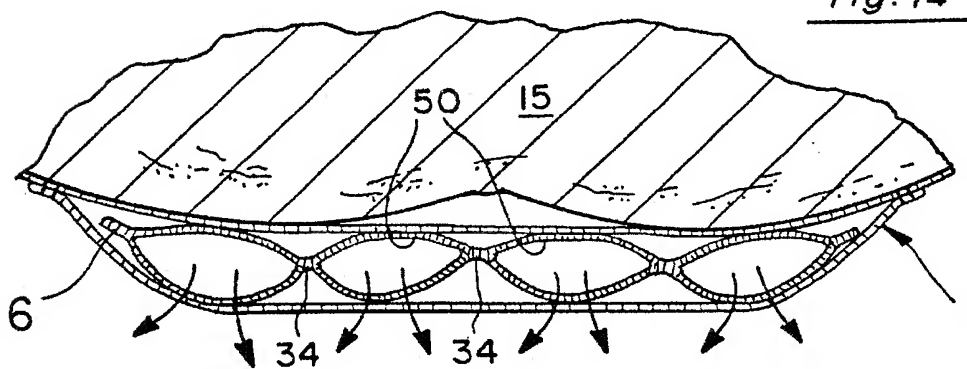


Fig. 15

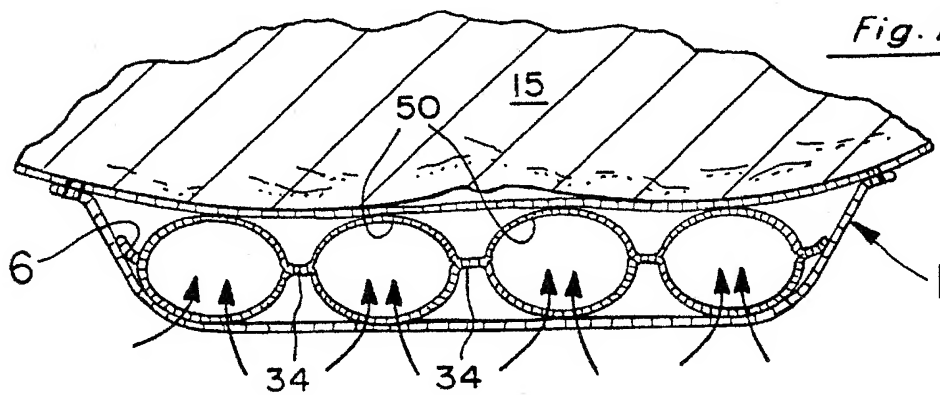


Fig. 16

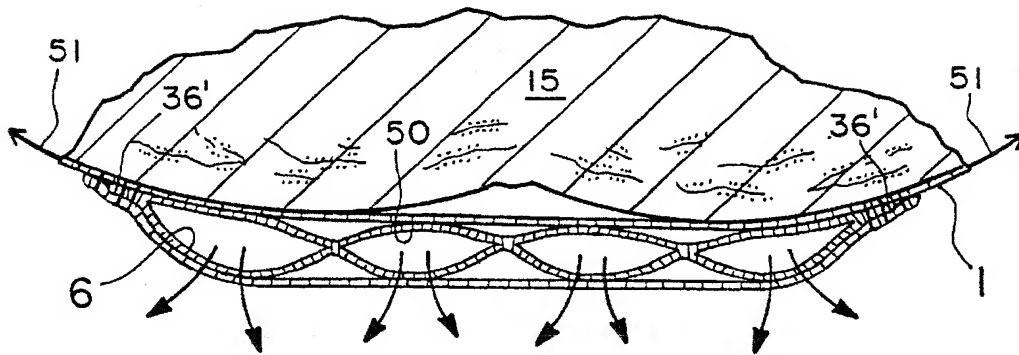


Fig. 17

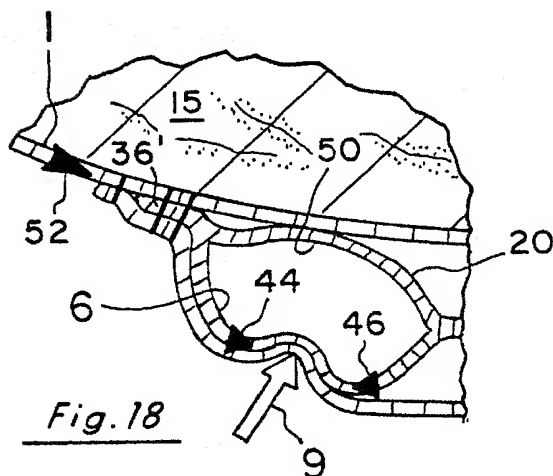
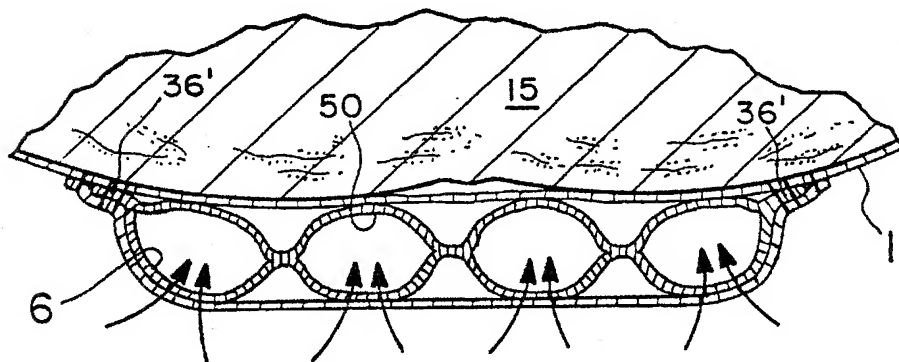


Fig. 18

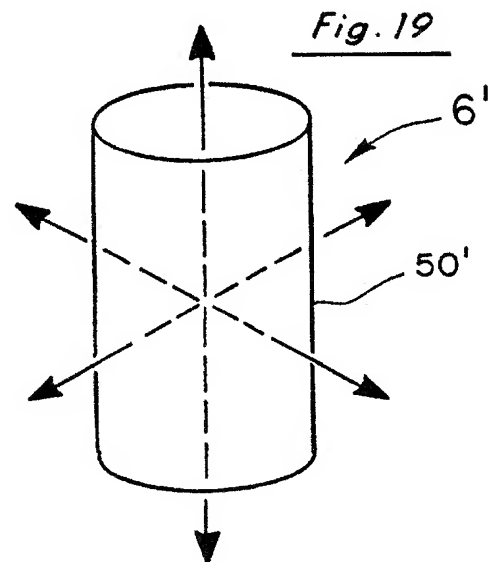
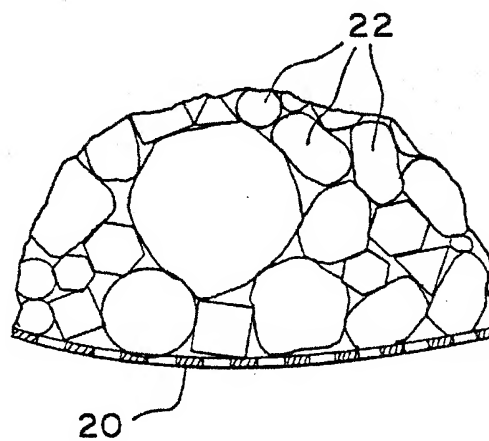
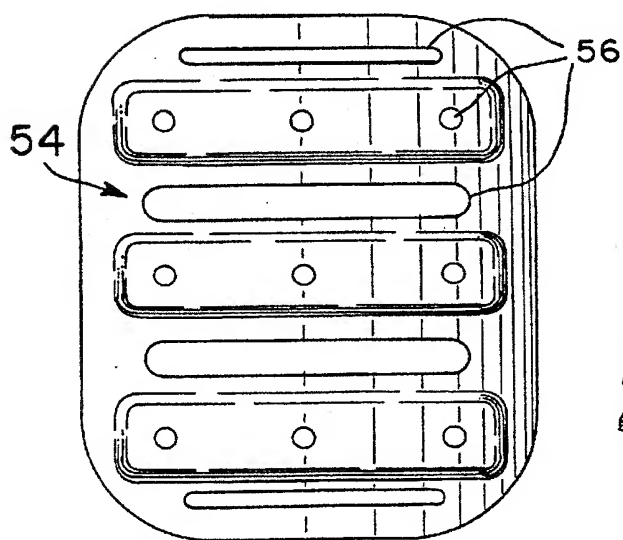
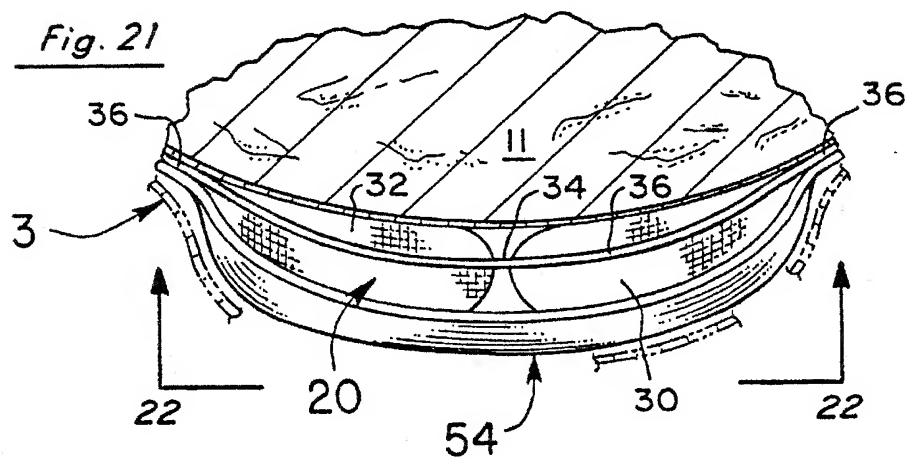
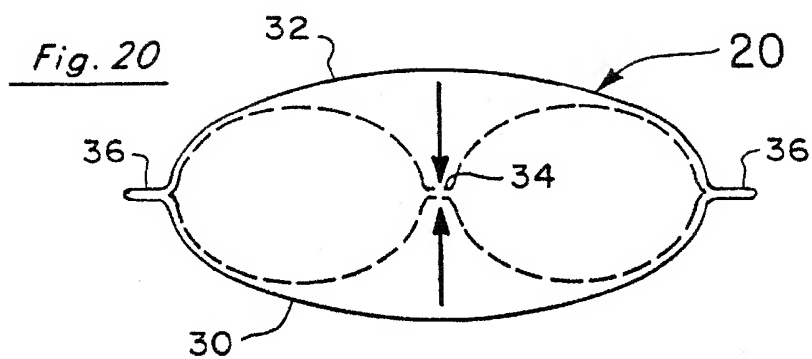


Fig. 19



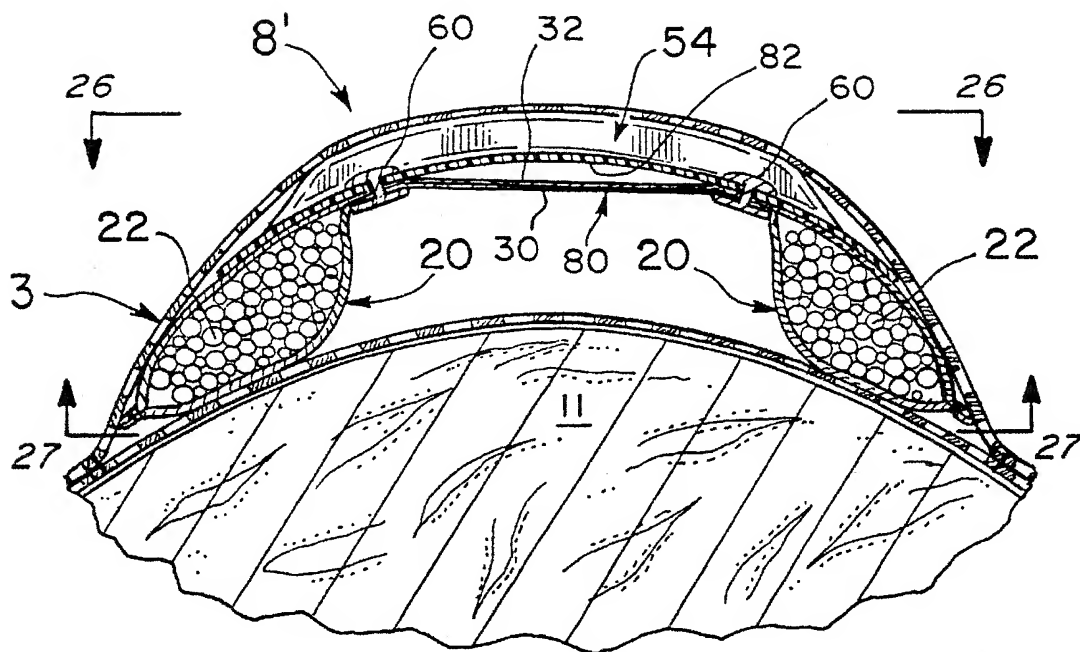


Fig. 24

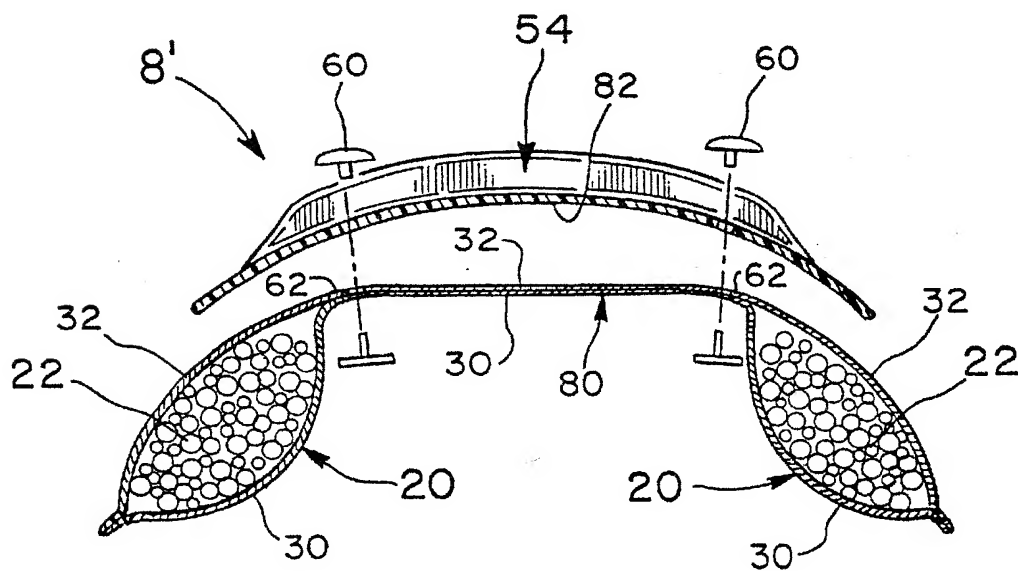


Fig. 25

Fig. 26

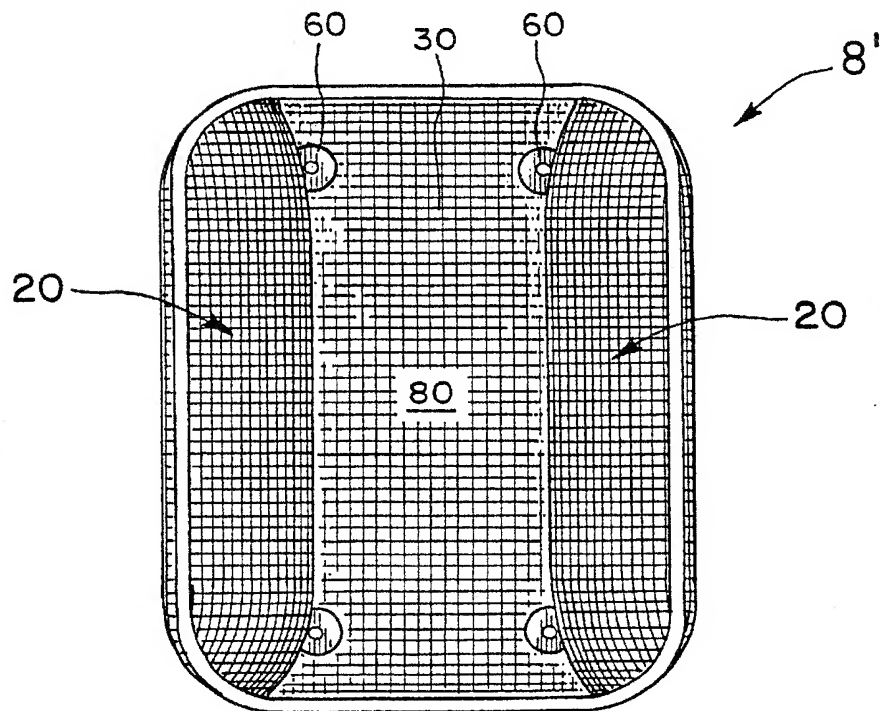
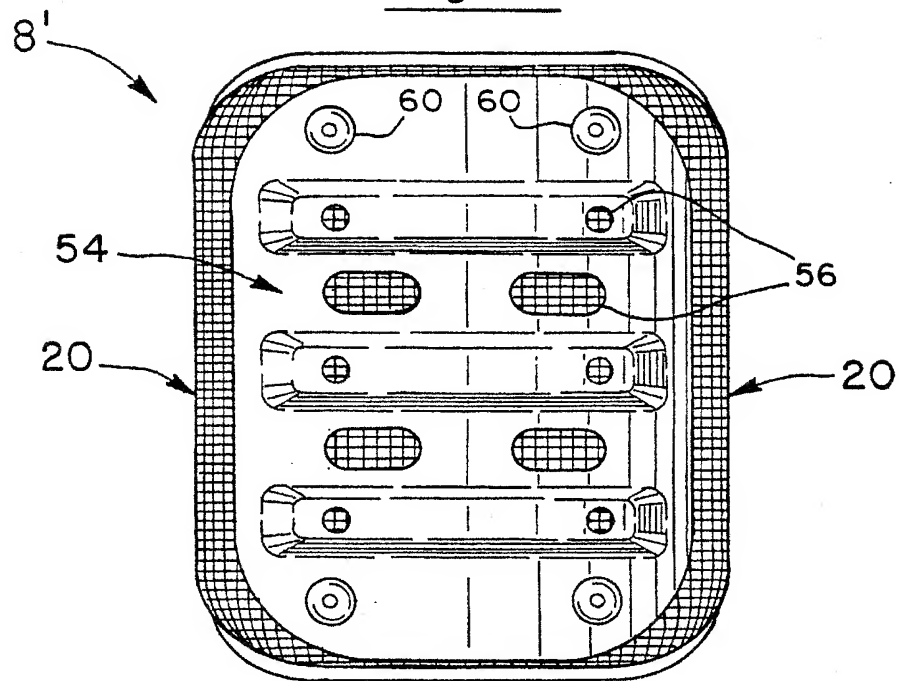


Fig. 27

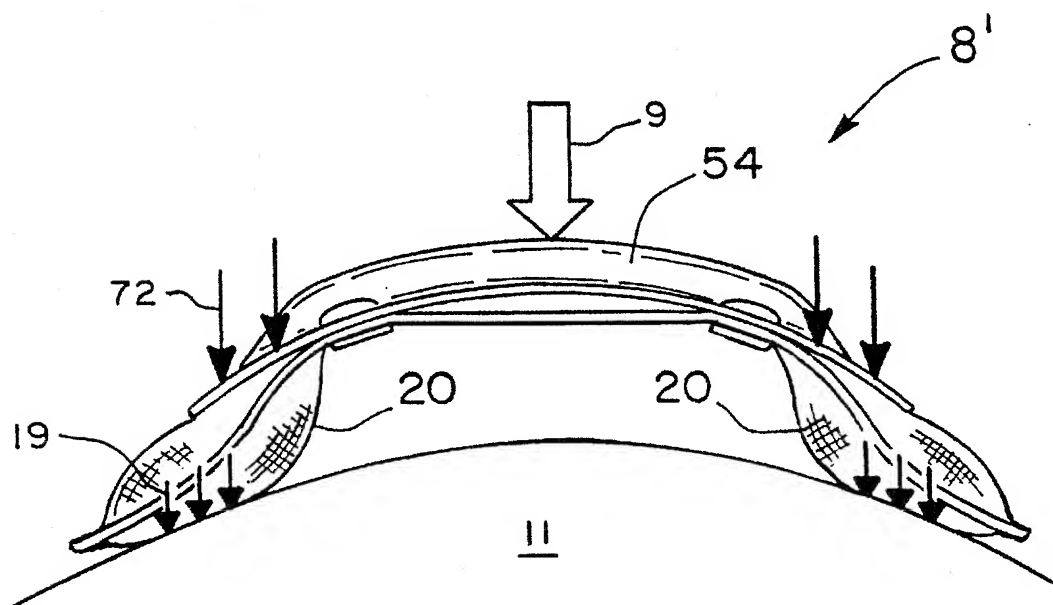
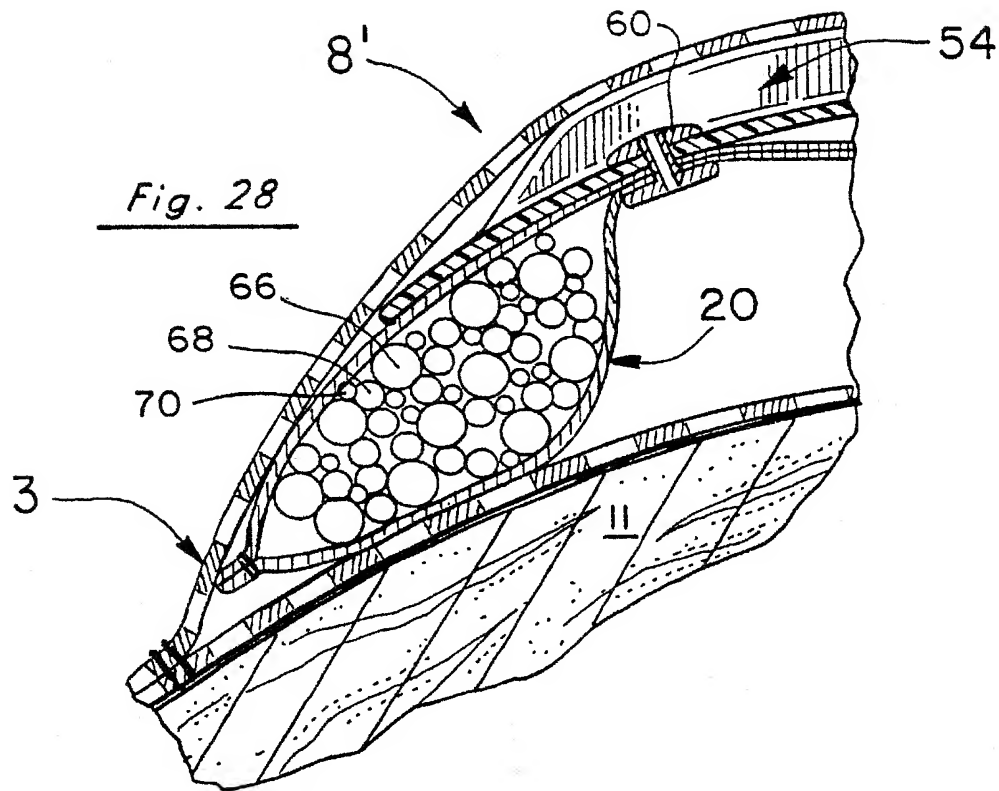


Fig. 29

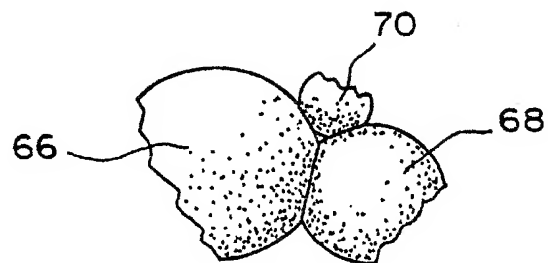
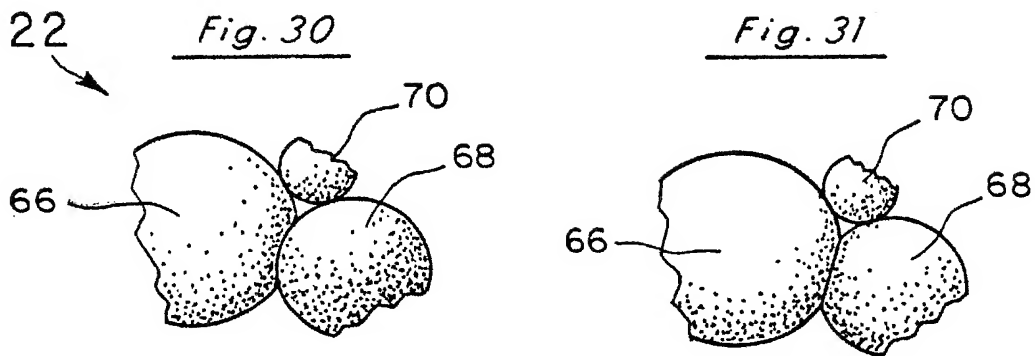
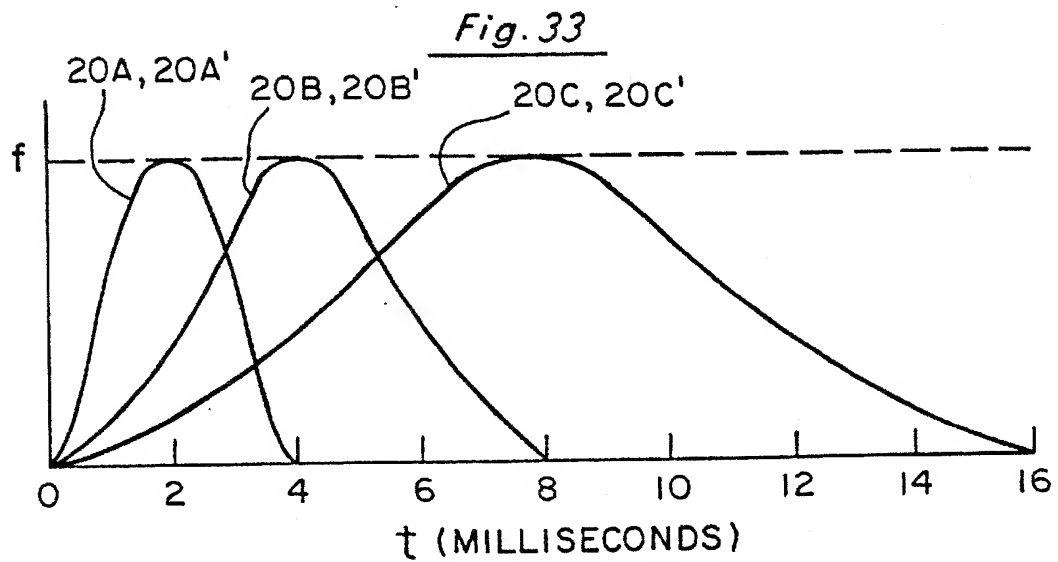
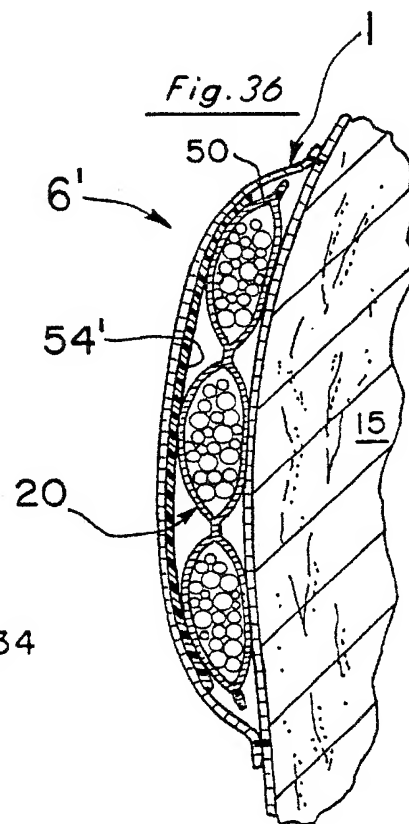
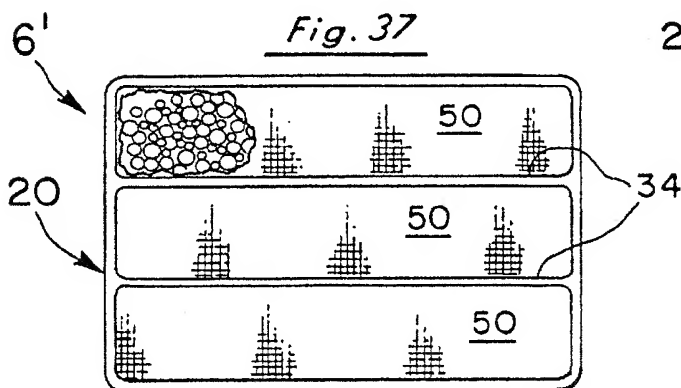
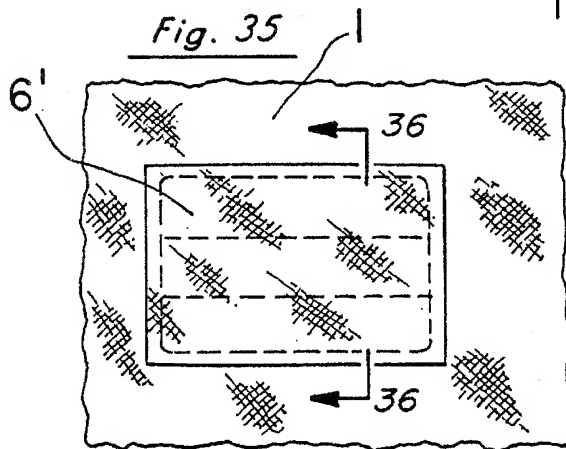
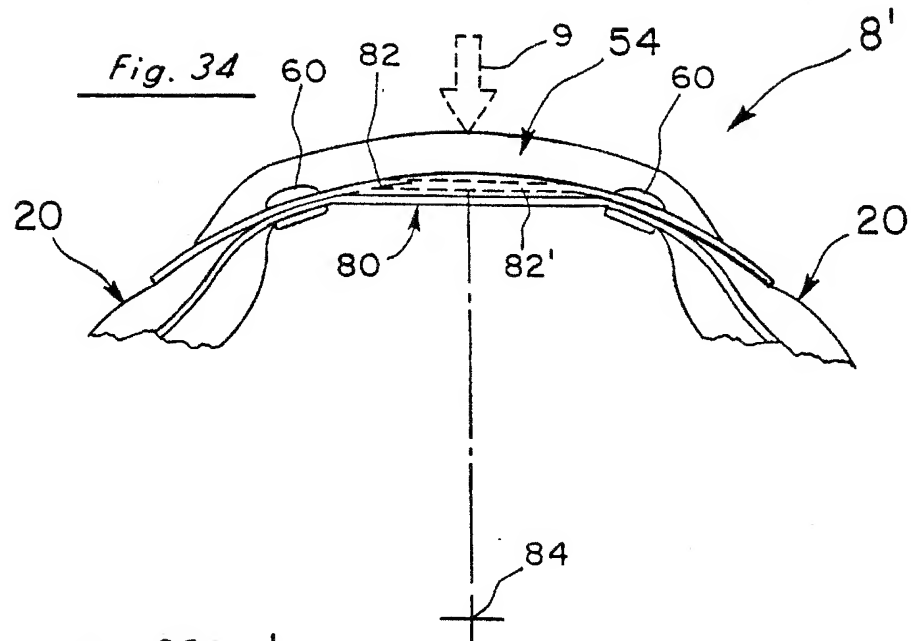
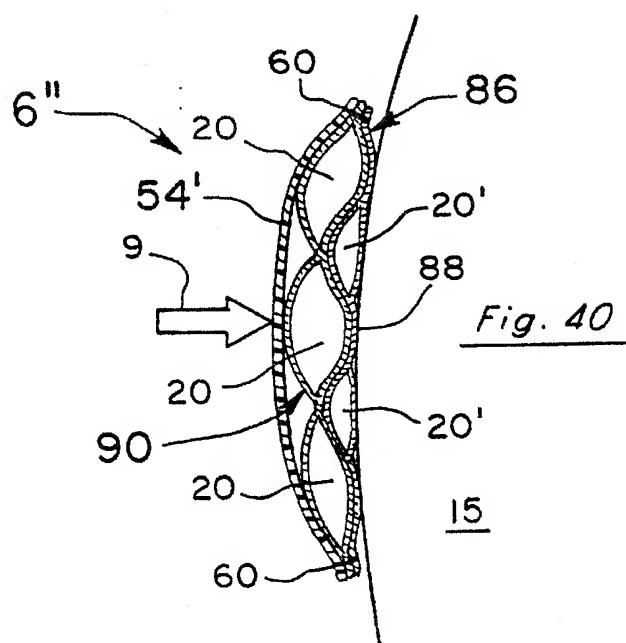
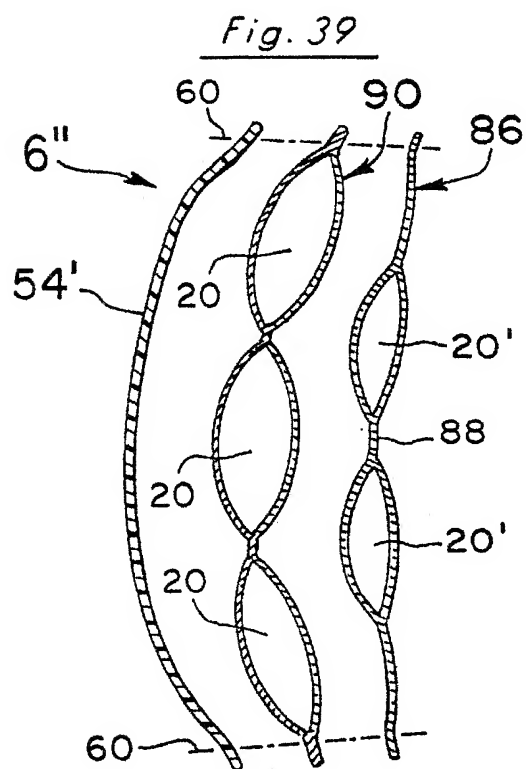
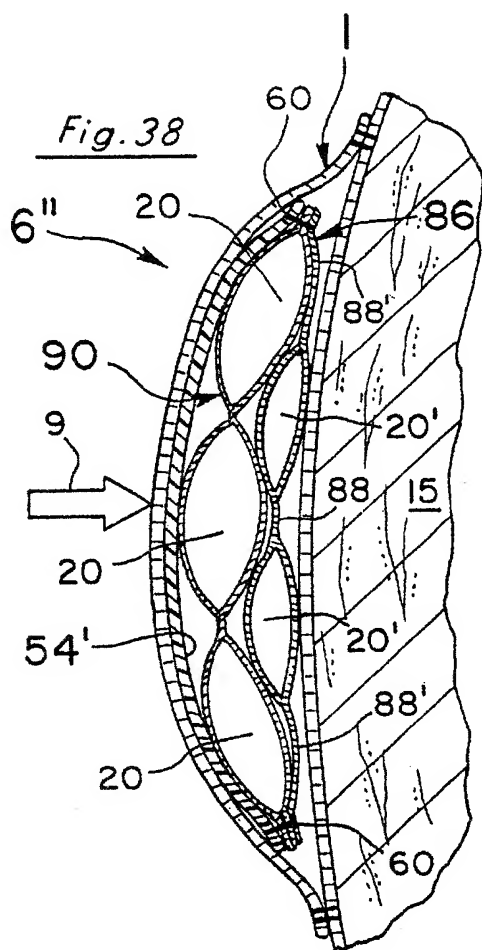


Fig. 32







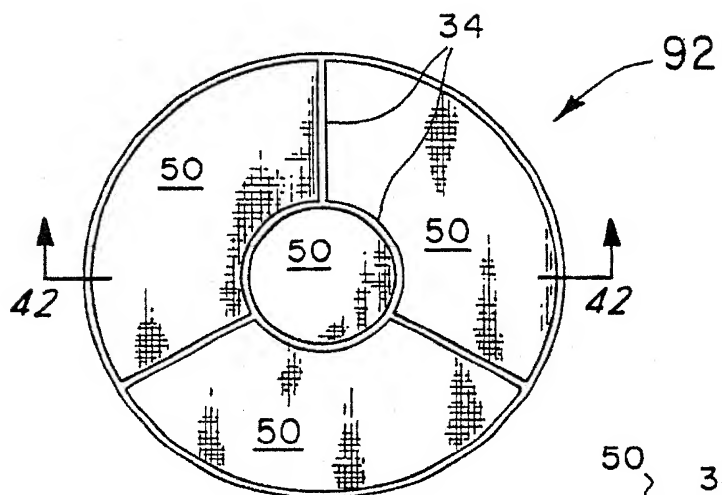


Fig. 41

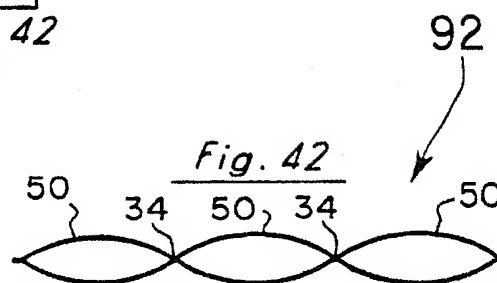


Fig. 42

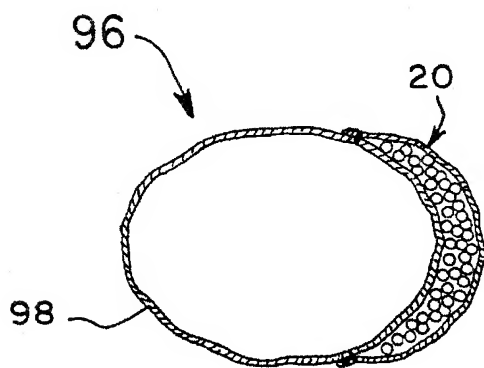


Fig. 43

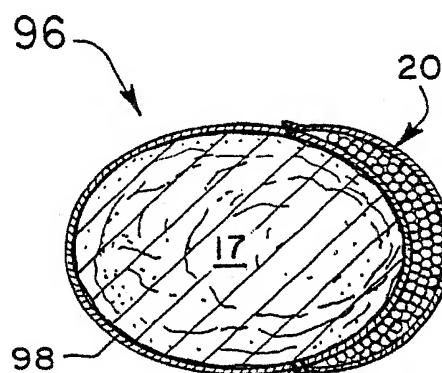


Fig. 44

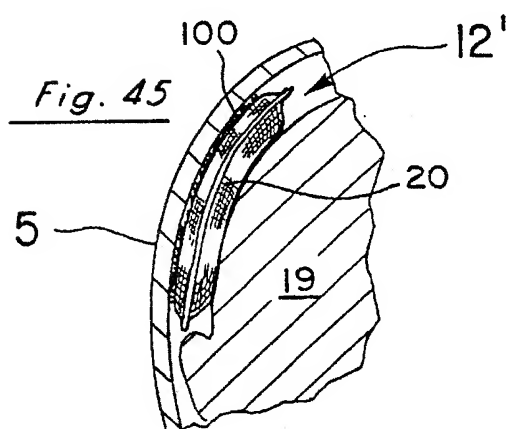


Fig. 45

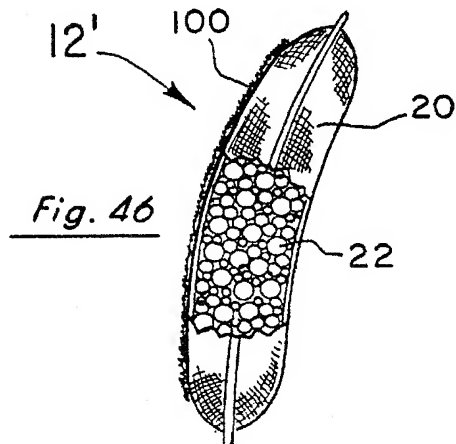
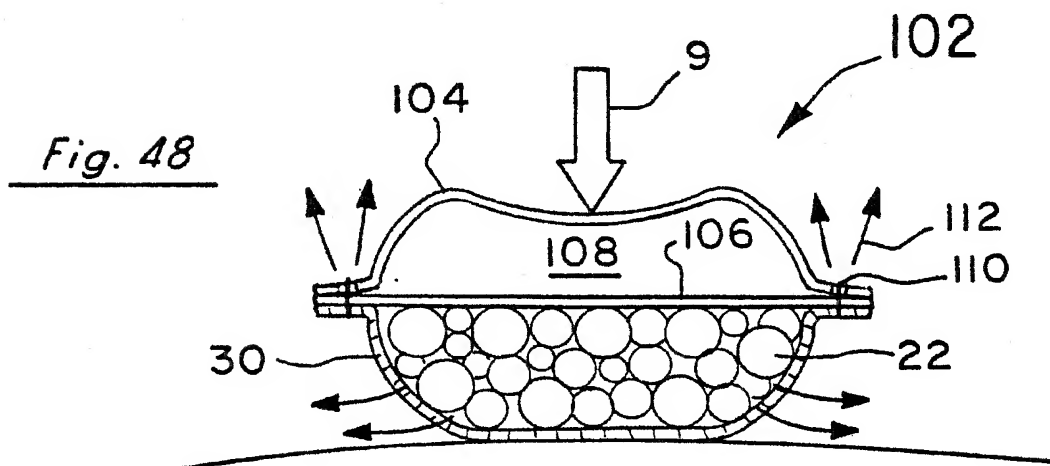
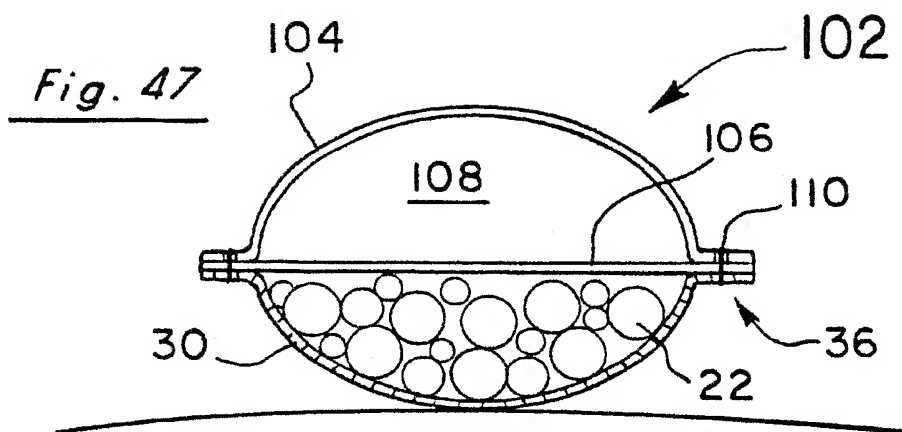


Fig. 46



PROTECTIVE PADDING FOR SPORTS GEAR

RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 09/506,507 filed Feb. 17, 2000 now U.S. Pat. No. 6,357,054, which is a continuation-in-part of U.S. patent application Ser. No. 09/226,311 filed Jan. 7, 1999, now U.S. Pat. No. 6,032,300, which is a continuation-in-part of U.S. patent application Ser. No. 09/158,088 filed Sep. 22, 1998, now U.S. Pat. No. 5,920,915.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the field of padding and more particularly, to the field of protective padding for sports gear.

2. Discussion of the Background

Designing protective padding for sports gear presents numerous challenges. In addition to having the padding perform its primary function of repeatedly absorbing and dissipating high impact forces, such padding would ideally be lightweight, breathable, and washable. Further, it would preferably be easily integrated into sports gear such as jerseys, pants, and helmets as well as be adaptable for specialized uses such as removable knee and elbow pads. All of the above would be accomplished in a manner that would not unduly inhibit the athlete's movements and dexterity on the field.

Many prior art pads and padding techniques accomplish some but not all of these goals. For example, U.S. Pat. No. 4,343,047 to Lazowski uses loosely filled, lightweight beads in a breathable casing to form a helmet pad. The helmet pad easily conforms to the contours of the wearer's head and in use, the loose beads are designed to move or shift around relative to each other within the casing. The beads are also designed to be crushed to absorb and attenuate high impact loads and forces. Such crushable padding is essentially effective for only one application and one impact situation, much like a car airbag in an emergency. As a practical matter, such padding cannot be used for other athletic gear such as football pants with thigh and knee pads that must withstand and be effective under repeated blows and impacts without losing their integrity.

Other prior art pads use incompressible beads that are designed not to be crushed (e.g., British Patent No. 1,378,494 to Bolton, U.S. Pat. No. 3,459,179 to Olesen, and U.S. Pat. No. 4,139,920 to Evans). Still others use compressible beads that are also designed not to be crushed such as U.S. Pat. No. 3,552,044 to Wiele and U.S. Pat. No. 5,079,787 to Pollman. However, in each case, the beads are loosely packed to allow the beads to move or roll relative to each other in an effort to achieve maximum conformation to the shape of the particular body part. Wiele in this regard even lubricates his beads to enhance their flowability. The thrust of these underfilled pads as expressed by Olesen, Wiele, and Pollman is to achieve padding with the flow and conforming characteristics of liquid-filled pads, but without the undesirable weight of such heavy fillings. Liquid-filled pads also necessarily require waterproof casings that make them unduly hot in use as they do not breathe. While such pads of loosely filled beads essentially conform like a liquid, the underfilled beads in them have an undesirable tendency to move out of the way in use. This tendency reduces the thickness of the padding around the body part and can even allow the body part to bottom out in the pad. In such a case,

the beads essentially move completely out of the way and the only protection left is simply the two layers of the casing for the pad. This is particularly true when used for impact padding where the blows tend to occur repeatedly at the same location. Such loose-filled pads for the most part are ineffective for such uses.

In the athletic field today, the standard padding used is one or more sheets or layers of foam. Foam in this regard has the distinct advantages of being lightweight and relatively inexpensive. For the most part, there are two types of such foam padding. The first is closed cell which has the advantage of not absorbing moisture or other fluids. However, layers of closed-cell foam tend to be stiff and do not conform well to the body, particularly when the athlete is active. They also do not breathe to dissipate body heat and generally cannot be sewn into or washable with the athlete's uniform. The second type of commonly used foam is opened cell. These foams tend to be softer and more pliable than closed cell foams; however, they absorb moisture and odor and generally need to be coated with a waterproof material (e.g., vinyl). This coating then makes the pads non-breathable and very hot.

With these and other concerns in mind, the padding of the present invention was developed and specifically adapted for use in sports gear. The padding of the present invention involves both overfilled pads (i.e., filled more than a simple gravity fill or 100% full) and pads with no more than a gravity fill. Both sets of pads can be used alone or with hard, outer shells; however, most of the overfilled applications do not use a hard, outer shell while most of the gravity filled (and under gravity filled) applications are preferably used in combination with a hard, outer shell. In the preferred embodiments of the overfilled, gravity filled, and under gravity filled padding, the adjacent beads within the pads preferably maintain their relative positioning in use (i.e., they do not flow or migrate relative to each other). The beads in this regard essentially maintain or stay in their positions relative to each other and just vary their degree or amount of compression. This in turn helps to prevent the pads from bottoming out in use. The present padding is lightweight, breathable, and washable. It can also be easily incorporated to protect a variety of body parts, all without unduly inhibiting the athlete's movements and actions. The padding is relatively simple and inexpensive to manufacture and can be easily integrated into nearly all sports gear.

SUMMARY OF THE INVENTION

This invention involves protective padding primarily intended for use in sports gear. In a first set of preferred embodiments, the pads include flexible, outer casings of porous, breathable, inelastic material overfilled with resilient, discrete beads of elastic material. The beads are initially in compressed states within the casing and place the outer, inelastic casing in tension. When a blow or force is applied, the beads are further compressed to absorb and dissipate the impact. Additionally, the applied blow or force will increase the tension in the outer casing to even further compress the elastic beads for better absorption and dissipation of the impact. In use, the porous pads are compressed and rebound to create a pumping effect that circulates air into and out of the pads drawing heat and perspiration from the athlete's body and keeping the athlete cool and dry. If desired, the pads can be secured directly to the athlete's jersey or other article of clothing to enhance this pumping effect as well as the dissipation of the force of any impact. In an alternate embodiment, the outer casing is made of an elastic material that is overfilled to its elastic limit to act in

the manner of the preferred embodiments. In a second set of preferred embodiments, the outer casings of the pads are actually filled no more than a simple gravity fill (i.e., 100%) and preferably are underfilled (e.g., 90%) to less than a gravity fill. This second set of pads is preferably used in combination with a hard, outer shell. Variations of the basic features of the first and second sets of pads are also disclosed. All of the pads of the present invention are lightweight and washable and can be adapted and integrated into a wide variety of items.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the padding technology of the present invention adapted and integrated into sports gear for football.

FIG. 2 is a cross-sectional view of the thigh pad of FIG. 1 taken along line 2—2 of FIG. 1.

FIG. 3 is an enlarged, cutaway view of the pad of FIG. 2 showing the initially compressed state of the beads in it.

FIG. 4 is a further illustration of the pad of FIG. 2 showing its segmenting.

FIG. 5 is a cross-sectional view taken along line 5—5 of FIG. 4.

FIG. 6 illustrates the knee pad of FIG. 1 incorporating the padding technology of the present invention.

FIG. 7 is a cross-sectional view taken along line 7—7 of FIG. 6.

FIG. 8 is a cross-sectional view taken along line 8—8 of FIG. 6.

FIG. 9 is an enlarged view of the pad of FIG. 2 initially receiving a blow or impact.

FIG. 10 schematically illustrates the increased compression forces applied by the casing as it is further tensioned by the applied blow.

FIG. 11 schematically shows the dissipation and reduction of the applied blow as received by the athlete's body.

FIG. 12 illustrates a pad of the present invention with a single pouch that has a substantially circular cross section.

FIG. 13 shows the sternum pad of FIG. 1 incorporating the padding technology of the present invention.

FIG. 14 is cross-sectional view taken along line 14—14 of FIGS. 1 and 13 showing the pouches of the pad substantially compressed to pump air out of them.

FIG. 15 is a view similar to FIG. 14 showing the pouches of the pad rebounding to their initial shape and volume to draw ambient air into them.

FIGS. 16 and 17 are views similar to FIGS. 14 and 15 with boundary portions of the pad attached to the jersey to further enhance the pumping action.

FIG. 18 illustrates an additional advantage of securing the pad to the jersey wherein the jersey is pulled or drawn in by the pad to further dissipate the force of any impact.

FIG. 19 schematically illustrates the multi-directional movement of air into and out of the pads of the present invention.

FIG. 20 illustrates one method of making the overfilled pads of the present invention.

FIG. 21 shows a pad according to the present invention used in combination with an outer, hard shell.

FIG. 22 is a view taken along line 22—22 of FIG. 21.

FIG. 23 illustrates the use of discrete beads of different shapes and sizes.

FIG. 24 illustrates a second set of protective padding of the present invention in which the pad casings are preferably

underfilled (or at least filled no more than a gravity fill) and are preferably used in combination with hard, outer shells. FIG. 24 in this regard is a view taken along line 24—24 of FIG. 1 showing thigh padding constructed in accordance with this second set.

FIG. 25 is an exploded view of the thigh padding of FIG. 24.

FIG. 26 is a view taken along line 26—26 of FIG. 24.

FIG. 27 is a view taken along line 27—27 of FIG. 24.

FIG. 28 is an enlarged view of one of the beaded casings of FIG. 24.

FIG. 29 is a view similar to FIG. 24 showing the result of the thigh padding of FIG. 24 receiving a blow or force.

FIGS. 30—32 illustrate the manner in which the differently sized beads progressively compress to progressively absorb forces applied to them.

FIG. 33 schematically shows how softer beads and less filled casings delay the transfer time of the applied force to the athlete's body.

FIG. 34 is a view similar to FIG. 24 showing a reinforcing characteristic of the pontoon shape of the thigh padding.

FIGS. 35—37 illustrate the application of features of the present invention to chest or sternum padding.

FIGS. 38—40 show further modifications to the basic structure of FIGS. 35—37.

FIGS. 41—42 show the present invention adapted for use in a doughnut shaped pad.

FIGS. 43—44 illustrate a method in which an overfilled casing can be created from an initially unfilled or gravity filled one.

FIGS. 45—46 show a modified pad in which the beads are fused together into a desired shape.

FIGS. 47—48 illustrate a modified pad in which the upper half is a waterproof and airtight compartment filled with open-cell foam and the lower half is a porous compartment filled with closed-cell, foam beads.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 illustrates the padding technology of the present invention adapted and integrated into sports gear for football. The particular gear shown in FIG. 1 includes an under or liner jersey 1 with upper arm 2, rib 4, and sternum 6 pads. The illustrated gear also includes liner pants 3 with thigh 8 and knee 10 pads and helmet 5 with head pads 12. Liner gear such as jersey 1 and pants 3 are commonly worn by football players next to their bodies. Full shoulder pads and exterior or playing jerseys and pants are then worn over the liner gear and can also be padded according to the present invention. The current technology additionally can be easily adapted for use in nearly any and all other types of padding including separate and removable ones such as elbow 14 and forearm 16 pads in FIG. 1.

The basic structure of the first set of protective pads of FIGS. 1—23 of the present invention as typified by the thigh pad 8 in FIGS. 1 and 2 includes an outer casing 20 (see FIG. 2) which is overfilled with beads 22. In use, the entire pad 8 is then received or sewn into a pocket in the pants 3. The outer casing 20 of the pad 8 is preferably made of a porous, breathable, and flexible material that is substantially inelastic. In the preferred embodiment, the casing 20 is a plastic mesh of a substantially waterproof material as polypropylene which is heat sealable. Other substantially inelastic, porous, and flexible materials could also be used if desired

5

such as woven or unwoven fiberglass, polyester, or nylon yarns preferably coated with PVC to make them heat sealable and waterproof. The casing 20 is overfilled with soft, resilient, discrete beads 22 of elastic material. The beads 22 are also preferably made of lightweight and waterproof material (e.g., a closed-cell foam such as polypropylene). In this manner and although the pad 8 is extremely porous, the casing 20 and beads 22 of the pad 8 do not absorb water, other liquids, or odors and the entire pad 8 can be washed and dried with the pants 3 and the rest of the gear of FIG. 1. The beads 22 can be of a variety of different shapes and sizes but preferably are spherical beads ranging in diameter from about 0.05 to about 0.5 inches. Depending upon the application, the beads could be smaller or larger but would still have the operating characteristics discussed below. The pores of the outer casing 20 are preferably as large as possible without allowing the beads 22 to pass through them during use.

The beads 22 are overfilled in the casing 20 meaning that the fill is higher than a simple gravity fill. Consequently, substantially all of the resilient beads 22 are in compression. The actual overfill above 100% can be up to 160% or more but is preferably about 120%. As illustrated in the enlarged view of FIG. 3, this leaves the compressed, spherical beads 22 of the preferred embodiments slightly distorted or flattened on the abutting portions 24 while the spaced-apart portions create the interstitial spaces 26 therebetween. Each bead 22 is thus compressed to under 100% to about 40% of its relaxed, uncompressed volume. Preferably, the compression is about 80% of the relaxed volume. The total volume of the interstitial spaces 26 under a gravity fill can be on the order of 35% of the casing volume. With the beads 22 initially compressed, this interstitial volume is then less than about 35% down to about 5% of the volume of the casing 20. Preferably, the interstitial volume is about 25%–30% of the casing volume with the compressed beads 22 then occupying the remaining volume of the casing 20.

The opposing portions 30 and 32 of the casing 20 in the thigh pad 8 as shown in FIGS. 4 and 5 are preferably segmented or joined by seams 34. Such segmenting or joining of the opposing portions 30 and 32 within the pad boundary 36 helps to prevent the pad 8 from ballooning. Depending upon the spacing of the segments 34, the cross-sectional shapes of the individually padded areas or pouches of the pad 8 can be varied to create nearly circular ones like 38 in FIG. 5 or more elongated ones such as shown in FIG. 2. (For clarity, the beads 22 are illustrated in FIG. 5 in only one of the pouches 38 but the beads 22 would be in all of the pouches 38.) The segmenting or joining at linear seams 34 also provides predetermined fold lines or patterns to help the pads conform better to the curved shapes of the user's body such as to his or her thigh 11 in FIG. 5. Such conformation gives the thigh pad 8 less of a tendency to rotate or otherwise move out of place. This is particularly important for the pads protecting joints such as the knee pad 10 in FIGS. 6–8. As illustrated the knee pad 10 is provided not only with a vertical segment or seam 34 but also with horizontal seams 40 and spot or dot attachments 42. Vertical segment 34 in FIG. 6 helps the knee pad 10 to conform about the knee 13 (FIG. 7) while the substantially perpendicular or horizontal segments 40 (FIG. 8) aid the pad 10 to bend with the natural flex of the knee joint. Spot or dot attachments 42 help to keep the pad 10 from ballooning.

The initially compressed beads 22 of FIGS. 2 and 3 within the casing 20 serve to place the outer, inelastic casing 20 in tension. This has the beneficial result of aiding in the absorption and dissipation of any blow applied to the pad.

6

More specifically and referring to FIG. 9 (in which only the pad 8 and athlete's thigh 11 are shown for clarity), any impact or blow 9 to the casing 20 will depress the inelastic casing 20 at the point of the blow 9. This depression in turn will draw in the casing 20 immediately to the sides 44 and 46 of the blow 9. The force applied by the blow 9 in FIG. 9 will then be absorbed and dissipated by the beads 22' directly under the blow 9 and by the surrounding beads 22", which will be further compressed by the increased tension in the casing 20 as explained below.

More specifically, the beads 22' directly under the blow 9 in FIG. 9 will first and foremost be further compressed by the blow 9 from their initially compressed state as in FIG. 3 to that of FIG. 9. These further compressed beads 22' at the point of blow 9 in FIG. 9 will then send or radiate compressive forces 9' outwardly to the remaining beads 22". These remaining or surrounding beads 22" in turn will be further compressed from their initial states by the radiating forces 9' acting on the beads 22" against the retaining force of the inelastic casing 20. This radiating action is essentially an inside-out one. Additionally, and because the casing 20 is inelastic and does not stretch, the blow 9 will draw in the casing 20 immediately to the sides 44 and 46 of the blow 9. This movement of sides 44 and 46 will reduce the casing volume and further tension the casing 20. It will also cause the casing 20 to increase the compression of the beads 22", essentially by applying forces 9" as illustrated in FIG. 10 from the outside-in. In these manners, the initial force of the blow 9 will be absorbed and dissipated within the pad 8 and the forces actually transferred to the athlete will be greatly reduced as schematically illustrated by forces 19 in FIG. 11. Preliminary tests show this reduction to be quite significant over the currently most popular pads and padding. Further, because of the resiliency of the discrete beads 22' and 22" in FIG. 9, the propagation of the force through the pad 8 is slower than through a pad, for example, composed of simply a layer of foam. This slower propagation speed helps to further dissipate the impact.

In use, the pads of the present invention offer still other unique advantages. Because the pads are overfilled and the casings initially tensioned, the pads are biased toward a first shape and volume. That is, when unimpeded by any external forces, each pad will assume a first, predetermined shape such as the symmetrical one illustrated in FIG. 12. Depending upon the amount of overfill of the beads 22 and other factors such as the relative stiffness of the casing 20 and the relative spacing of any segments 34, the unrestrained, single pouch 50 of the pad in FIG. 12 tends toward a nearly circular cross section. Even under mild restraints such as the pants 3 on the motionless athlete of FIGS. 1 and 5, the multiple pouches 38 of the thigh pad 8 in FIG. 5 are still individually biased toward a first or free shape such as in FIG. 12. Such bias for the most part is provided by the outwardly directed forces of the compressed beads 22 acting against each other and against the flexible but inelastic, outer casing 20.

In a like manner, even the more flattened or elongated pouch of pad 8 in FIGS. 2 and 10 is biased toward a first shape and volume. Consequently, if a blow such as 9 in FIG. 10 is delivered compressing the pad 8 (as shown in dotted lines in schematic FIG. 10), the pad 8 upon dissipation of the blow 9 will automatically rebound to the original shape and volume shown in solid lines in FIG. 10. (For clarity, only the athlete's thigh 11 and the elongated pouch of pad 8 are shown in this schematic FIG. 10.) Because the casing 20 is porous and breathable and because the compressible beads 22 form interstitial spaces 26, this action on the pad 8 will have a desirable pumping effect. Such effect will force or

pump air out of the pad 8 during the compression of blow 9 and draw in ambient air during the return or rebound toward the original shape.

This pumping effect also occurs with any natural movement of the athlete that tends to further compress and then release the pad (e.g., flexing and unflexing the knee in FIG. 8 during running). Such movement, as with a blow, first compresses the beads 22 further and reduces the total volumes of the casing 20 and the interstitial spaces 26. The resilient beads 22 then rebound to their initial state and volume returning the casing 20 and interstitial spaces 26 to their original volumes. This action is a pumping one and has its most beneficial effect around the jersey 1 to help dissipate and draw or wick away the athlete's body heat and perspiration. More specifically and referring to the chest or sternum pad 6 of FIGS. 1 and 13, the pad 6 would typically have a plurality of individual, completely compartmentalized pouches 50 (see FIG. 13). These individual pouches 50 would be separated by vertical and horizontal seams 34 and 40. In use as illustrated schematically in FIG. 14 and 15 (in which the pouch beads are not shown for clarity), the pouches 50 of the pad 6 alternately expel and draw in air. That is, at maximum inhalation or movement, the lateral or side-by-side array of pouches 50 in the jersey pocket 1 in FIG. 14 would assume compressed positions or shapes pumping air along with body heat and perspiration out of the pouches 50 and through the porous, mesh jersey 1. During simple breathing, this compression is caused primarily by the already tightly fitting jersey 1 being drawn even tighter about the athlete's chest 15 during inhalation. Upon exhaling, the pouches 50 naturally return or rebound to the positions of FIG. 15 drawing or pumping in ambient air. With each breath and/or movement, the process is repeated, cooling and drying the athlete's body.

To further enhance the pumping effect of the pads of the present invention, boundary or other spaced-apart portions of the pads can be secured if desired to move with the particular article of clothing such as jersey 1. For example, by actually sewing or otherwise securing opposing boundary portions 36' of the pad 6 in FIGS. 16 and 17 to spaced-apart portions of the flexible jersey 1, the stretch or pull of the elastic jersey 1 at 51 during even normal breathing will enhance the contraction of the pad 6 (FIG. 16) and its overall pumping action (FIGS. 16-17). Such securing also helps to keep the particular pad firmly and properly in place in the jersey 1 or other article or articles of clothing (such as items 3, 5, 14, and 16 of FIG. 1, or similar ones).

Further, the securing of the pad such as 6 in FIGS. 16 and 17 to the jersey 1 integrates the jersey 1 into the pad 6 and in essence makes the jersey an extension of the pad casing 20. Consequently, during an impact 9 as in FIG. 18, the casing 20 reacts in the manner of FIG. 9 drawing in the casing sides 44 and 46 immediately adjacent the blow 9; and, because the inelastic casing 20 is secured at each side 36' to the jersey 1, the jersey 1 is also drawn in at 52. The jersey 1 about the athlete's chest 15 then acts with and under the influence of the casing 20 to further dissipate the force of the impact 9. The impact 9 in FIG. 18 is shown striking the far left pouch 50 for illustrative purposes. However, depending upon where the impact strikes across the pad 6 and how broad the impact is, the jersey 1 would be pulled or drawn in to different degrees from all directions or sides 36' about the pad 6. If the pad 6 is secured to the jersey 1 as in FIGS. 16-17, it can be done so directly without the need to form a pocket in the jersey 1 as in these FIGS. 16-17.

It is noted that FIGS. 16 and 17 schematically illustrate the pumping action of the pad 6 with arrows directed

primarily away from and toward the athlete's chest 15. However, the pads of the present invention including pad 6 with pouches 50 in FIGS. 16 and 17 are extremely porous in all directions. Consequently, as schematically shown in FIG. 19, the air moving into and out of the pouch 50' of pad 6' (and every pad of the present invention) travels in all directions. In contrast, for example, sheets of closed-cell foam that are perforated in the fashion of swiss cheese may pass air through the holes but cannot pass air laterally through the foam sheet. To the extent the sheet is made of open-celled foam to pass air in all directions, it then has the distinct disadvantage of absorbing moisture and odor.

As discussed above, the prestressed or initially compressed condition of the elastic beads 22 in the free state of FIG. 12 tensions the inelastic, outer casing 20. In use, this also helps to prevent the beads 22 from moving relative to each other. The beads 22 in this regard essentially maintain or stay in their positions relative to each other and just vary their degree or amount of compression. Consequently, the overfilled pads of the present invention will not bottom out in use. This is an important feature of the pads, particularly as used in sports gear. Comfort of the pad against the athlete's body is also a concern. To the extent the casing 20 is made of relatively stiff material or material that tends to be abrasive or irritating to the athlete's skin, the jersey 1 in FIGS. 14 and 15 acts as a soft barrier to the casing 20. In other applications such as forearm or shin guards, an additional layer of soft material could be added if desired to the pads of the present invention between the casing 20 and the athlete's body.

The overfilling of the pads to compress the beads 22 and tension the outer casing 20 can be accomplished in a number of manners. The preferred and simplest method is to substantially, or completely, gravity fill the casing 20 as shown in solid lines in FIG. 20. The opposing sides 30 and 32 of the casing 20 can then be depressed or pinched to form the segment 34 (shown in dotted lines in FIG. 20). Thereafter, the segment 34 can be joined by heat sealing the sides 30 and 32 of the casing 20 together or by some other method such as sewing, stapling, or riveting. The segment 34 in this regard can extend partially across the pad as in FIGS. 4 and 6 or completely across the pad as in FIGS. 13-15 to make separate and distinct pouches 50. Single or unsegmented pads such as the pad in FIG. 12 can be made by simply cutting the segmented pad of FIG. 20 along the joined portion or seam 34 to form separate, individual pads. Other techniques to overfill the pads could also be used such as blowing, screwing, or ramming the beads under pressure into the pad to compress the beads and sealing the pad shut while the beads remain compressed. Multiple compression steps can also be performed as for example initially compressing the beads 22 by one of the above techniques and then further compressing them by adding more linear segments 34 or spot joining the opposing sides 30 and 32 of casing 20 with staples or rivets.

The padding technology of the present invention is equally adaptable for use under hard, outer shells such as those normally used in football shoulder pads and thigh pads. In adding an outer, hard shell 54 as illustrated in FIGS. 21 and 22, the shell 54 is preferably well perforated (see perforations 56 in FIG. 22) so as not to unduly reduce the breathability of the underlying pad 8. In use, the pad 8 with the outer, hard, porous shell 54 essentially operates as described above except that the initial impact force is immediately dissipated by the shell 54 and spread or applied to the pad 8 across a larger area than in the case of FIGS. 9-11. Lighter, less hard coverings or outer layers could also

be used in place of the shell 54 if desired such as an additional mesh layer of relatively stiff material. The stiffness of the mesh of the casing 20 can also be varied as desired to be relatively soft or even approach the stiffness of a hard shell like 54. The stiffer the casing 20, the more it then acts like a hard shell 54 to spread out and dissipate the blow. When a hard shell 54 is used, it has been found desirable to use relatively soft beads 22 beneath the shell 54 so the overall padding does not become too hard. This is particularly advantageous in sports such as hockey in which nearly all the pads will have hard, outer shells 54. In such cases, the fact that air moves into and out of the pads in all directions (as schematically shown in FIG. 19) becomes very important as the hard shell 54, no matter how perforated or porous it is, tends to restrict air flow through it. However, with the pads of the present invention, the air movement then simply moves laterally or in all of the remaining directions not inhibited by the shell 54. In contrast as discussed above, closed-cell foam sheets perforated like Swiss cheese will have any air flow blocked by the shell and air cannot move laterally through the sheet. If the foam is made of open-celled foam, air may flow around the shell but the foam will then absorb moisture and odors.

While several embodiments of the present invention have been shown and described in detail, it is to be understood that various changes and modifications could be made without departing from the scope of the invention. For example, as mentioned above and illustrated in FIG. 23, the beads could be of different sizes and shapes (e.g., spheres, cubes, oblongs, pyramids, and cylinders). In this regard, it has been found with beads of closed-cell polypropylene, for example, that it is preferred to use smaller diameter beads (e.g., 0.125 inches) packed fairly tightly (e.g., 140% overfill) for areas in which impact absorption is paramount (e.g., knee). Conversely, larger diameter beads (0.25 inches) of polypropylene with less compaction (e.g., 110%–120%) have been found to work better for areas in which breathability is of primary importance, such as in the chest area, to dissipate the athlete's body heat. Such larger diameter beads of polypropylene also tend to be softer than smaller diameter ones. Other factors such as the stiffness of the casing 20 as discussed above can also be varied as desired. In this manner, pads using the technology of the present invention can be custom designed not only for particular uses but also for particular individuals.

Further, and although the casing 20 is preferably overfilled only with compressible beads 22, portions of the fill could be other items with other properties (e.g., incompressible) as long as the fill was predominantly of the preferred, resilient, elastic members or beads 22 to give the pads the desirable characteristics discussed above. Additionally, the casing 20 has been discussed above as being preferably made of inelastic material. However, the casing 20 can be made of an elastic material if desired that was also flexible, porous, and breathable. The elastic casing 20 would then be preferably overfilled and expanded substantially to its elastic limit to place the beads 22 in compression and the stretched casing 20 in tension. The casing 20 would then act substantially in the manner of an inelastic one and the overall pad would perform substantially as discussed above and as illustrated in FIGS. 1–23. It is further noted that the padding of the present invention has been primarily disclosed as adapted for use in sports gear but it is equally adaptable for use wherever foam and other padding are used. For example, the padding technology of the present invention could be used as pads for fences, poles, trees, and walls as well as in industrial applications such as elevators and vehicle bumpers.

Additionally, as best seen in FIGS. 24 and 25, a second set of protective padding of the present invention involves initially filling the inelastic casings 20 to no more than a simple gravity fill (i.e., 100%) and preferably underfilling the casings 20 to less (e.g., 90%) than a gravity fill. The casings 20 are then untensioned and substantially all of the beads 22 are uncompressed in the casings 20. This second set of protective padding with underfilled casings 20 (see FIGS. 24–27) is preferably used in combination with a hard, outer shell such as 54. Like the first set of protective padding of FIGS. 1–23, the casings 20 are preferably made of porous, breathable, and flexible material which is substantially inelastic. Similarly, the casing material is preferably a plastic mesh of a substantially waterproof material (e.g., polypropylene) that is heat sealable. The beads 22 are also preferably made of waterproof material (e.g., closed-cell, foam beads such as polypropylene). Like the pads of the first set of FIGS. 1–23, the casings 20 and beads 22 themselves do not absorb water; however, the overall pads themselves are extremely porous and breathable to help keep the athlete's body cool. In this regard, both air and water will easily pass or flow through the pad but will not be absorbed by any of its components, including the casings 20 and beads 22 of the pads.

FIG. 24 in this regard is a view taken along line 24–24 of FIG. 1 illustrating this second set of padding in use as thigh padding 8'. As shown, the padding 8' of FIG. 24 includes a hard, outer shell 54 to which the pair of casings 20 are attached by rivets 60. More specifically, as illustrated in the exploded view of FIG. 25, the two layers or portions 30 and 32 of the casings 20 are preferably heat sealed or sewn at 62 to form somewhat of a pontoon shape. Each pontoon casing 20 is then initially filled to no more than a gravity fill (i.e., 100%) and is preferably slightly underfilled (e.g., 80%–95% of a simple gravity fill). The casings 20 are preferably attached adjacent the joined areas 62 to the hard, outer shell 54. The shell 54 like the one of FIG. 22 is perforated at 56 (see FIG. 26) to be very porous so as not to unduly reduce the breathability of the overall padding 8'.

In the preferred embodiments of the second set of protective padding as typified by the padding 8' of FIGS. 24–27, the beads 22 are preferably blended and are a mix of different shapes as in FIG. 24 and/or at least two and preferably three, differently sized beads 66, 68, and 70 (see FIG. 28). The beads 66, 68, and 70 are preferably of grossly different sizes, as for example spheres with relative diameters of 1:2:3 (e.g., $\frac{1}{2}$: $\frac{1}{6}$: $\frac{1}{4}$ inches). When the beads are made of the same material (e.g., closed-cell polypropylene or polyethylene), the expanded size differences normally translate directly into varying degrees of softness (e.g., ease of compression). The largest beads 66 are then softer (e.g., have a lower spring coefficient) and compress more easily than the medium-sized, denser beads 68 which in turn are softer and compress more easily than the smallest and densest beads 70. Consequently, in use when a force or blow 9 is applied as in FIG. 29, the beads 66, 68, and 70 will normally progressively compress from beads 66 (FIG. 30), to beads 68 (FIG. 31), to beads 70 (FIG. 32) to progressively absorb the blow. However, if the applied force or blow 9 is fairly light, it may be that only the largest beads 66 are compressed. Similarly, if the force 9 is an intermediate one, beads 66 and 68 may only be compressed. Heavy forces 9 would then progressively compress all of the beads 66, 68, and 70.

Regardless of the size of the impact force 9 and/or how many differently sized beads 66, 68, and 70 are compressed, the combined effect of the hard, outer shell 54 and relatively

11

soft beads 66, 68, and 70 is at least two fold. First, it spreads out the applied force 9 and second, it extends or delays the transfer time of the applied force 9 through the padding 8' to the athlete's thigh 11. That is, the geometry of the hard shell 54 over the casings 20 in FIG. 29 will serve to spread out and dissipate the force 9 from the relatively small, impact area to the larger contact area between the casings 20 and the athlete's thigh 11. However, equally important in the overall design of the padding 8' of FIGS. 24-29 is the softness of the beads (whether or not a mix) in the casings 20. The beads in this regard are preferably soft enough that the initially reduced forces at 72 between the hard, outer shell 54 and beaded casings 20 in FIG. 29 will significantly compress the beads. Otherwise, the load of the impact force 9 will be transferred too quickly through the beaded casings 20 to the thigh 11 causing increased damage and injury (e.g., bruising). In contrast, the beaded casings 20 in the preferred embodiments of FIGS. 24-32 are as soft as possible to thereby be compressed by the forces 72 and extend the transfer time of the forces through the padding 8' as long as possible.

The empirical benefits of this extending or delaying of the transfer time of the forces through the padding 8' are to lessen the damage and injury to the athlete's body. This is schematically illustrated in FIG. 33. In this FIG. 33, the beaded casings are made progressively softer (e.g., more easily compressed) from casings 20A to 20B to 20C. Except for the softness of the beads, the beaded casings 20A, 20B, and 20C are otherwise identical. As shown, the transfer time *t* of the same, peak load or force *f* to the athlete's body for the softest, beaded casing 20C is essentially twice as long (e.g., 8 milliseconds) as for the less soft, beaded casing 20B (e.g., 4 milliseconds). Similarly, the least soft (i.e., hardest or firmest), beaded casing 20A has the quickest transfer time (e.g., 2 milliseconds) and is potentially the most damaging to the athlete. In making the beaded casing 20C as soft as possible, for example, the largest beads 66 in the mix would preferably be compressible with as little force as possible to 50% and preferably 20% of their relaxed or uncompressed volume. If made of the same material (e.g., polypropylene) as discussed above, the smaller beads 68 and 70 would not be as soft (e.g., would not be as easily compressed for any given force) but they still would preferably be very soft, easily compressible beads. Preferably, the beads are always made of a waterproof material (e.g., closed-cell foam of polypropylene or polyethylene).

FIG. 33 also schematically illustrates the benefit of underfilling the casings 20 (e.g., 80%-95% of a simple gravity fill). More specifically, FIG. 33 shows the force transfer delay for the thigh padding 8' configuration such as in FIG. 24 using an overfilled casing 20A', a gravity or 100% filled casing 20B', and an underfilled (e.g., 90% of a gravity filled) casing 20C'. Except for the degree of fill, the casings 20A', 20B', and 20C' in FIG. 33 are otherwise identical. The combined teachings of FIG. 33 is that in padding using a hard, outer shell 54, casings 20 that are underfilled (e.g., 90%) with the softest beads are preferred. This is not to say that overfilled casings 20 as in FIGS. 1-19 are not desirable when the protective padding has no hard, outer shell 54. In fact, such overfilled casings 20 are preferable over gravity filled or underfilled casings 20 if used alone without a hard, outer shell 54. However, when used with such a shell 54, overfilled casings 20 are less desirable than gravity filled ones which in turn are less desirable than slightly underfilled (e.g., 80%-95%) ones due primarily to the delayed transfer time effect discussed above.

In actual operation, the final stages of the transfer of the impact force 9 in FIG. 29 to the athlete's thigh 11 with an

12

initially underfilled (e.g., 90%) casing 20 is essentially the same as discussed in regard to the overfilled casing 20 of FIGS. 9-11. The same is true for a gravity filled one. In other words, the underfilled or gravity filled casings 20 under a hard, outer shell 54 will distort to a smaller volume shape under the applied force 9 (compare the casings 20 of FIG. 24 to the more flattened ones of FIG. 29). This will essentially compress the beads 66, 68, and 70 and tension the inelastic casing 20 to thereafter operate in the manner of the initially overfilled casing 20 of FIGS. 1-23. However, as discussed above, the underfilled (and to a lesser extent the gravity filled) casings 20 will reach this state more slowly than an initially overfilled casing 20 (using the identical beads or bead mix).

Returning to the blending or mixing of bead sizes 66, 68, and 70 in FIG. 28, this offers several advantages. As discussed above, it creates a gradient of softnesses and a progression of bead compressions from the largest beads 66 down to the smallest beads 70. Additionally, and perhaps more importantly, such blending or mixing inhibits migration or movement of the beads relative to each other. This is true for overfilled, gravity filled, and underfilled casings 20 but is particularly important for underfilled ones. By blending the beads, the volume of the individual voids or interstitial spaces is reduced. This in turn inhibits bead migration by physically making it more difficult for the beads 66, 68, and 70 to move relative to each other as there simply is less space or room to do so. The volume of such voids or interstitial spaces might, for example, be reduced 10% to 25% by such mixing. The result is that adjacent beads within each pad casing 20 assume initial positions relative to each other after the casing 20 is initially filled and maintain their initial, relative positioning in use (i.e., the beads do not flow or migrate relative to each other). The beads in this regard essentially maintain or stay in the same, initial positions relative to each other and just vary their degree or amount of compression. This in turn helps to prevent the pad casings 20 from bottoming out in use. Such migration can also be inhibited by increasing the surface friction (e.g., roughness) of the beads (whether a mix or not) and by increasing the surface friction of the material of the outer casing 20 itself. The mesh size of the material of the outer casing 20 can also be varied so that portions of the beads actually protrude or stick through and become caught up in the mesh. Using stiffer material for the casings 20 will also help as will segmenting. Nevertheless, even without blending, it is noted that the beads will tend to clump, plug, or bridge against each other as illustrated in the lower left portion of FIG. 28. This not only inhibits migration of the beads but also helps create desirable voids in underfilled casings, as also best illustrated in the lower left portion of the underfilled casing 20 of FIG. 28.

FIG. 34 illustrates another aspect of the pontoon shape of the casings 20 of FIG. 24-25 in which the central portion 80 of the pontoon shape helps to reinforce the hard, outer shell 54. More specifically, the central portion 80 (i.e., the central portions or sides 30 and 32 of the flexible, inelastic material of casings 20 of FIG. 25) is attached at 60 to extend across the curved or arched, inner surface 82 of the hard shell 54 (see FIG. 24). The distance along the arched, concave, inner surface 82 about the axis 84 in FIG. 34 between the sections of the shell 54 at rivets 60 is then greater than the chord distance between the spaced-apart portions of 80 attached to the shell 54 at rivets 60. The chord-like portion 80 is preferably prestressed or pretensioned but can be simply taut if desired. Since the material of 80 is preferably inelastic and does not stretch, any force 9 applied in FIG. 34 tending to

13

flatten the arch of surface 82 (e.g., toward the position 82' shown in dotted lines in FIG. 34) will be resisted by the piece of material 80. If desired, the portion 80 could be slightly loose if desired to then assume a taut or tightened condition upon any flattening movement of the arch at 82. Although preferably inelastic, the material of 80 could be elastic if desired and still act to reinforce the arched shape 82 of the shell 54.

FIGS. 35-37 illustrate a modified chest or sternum padding 6'. In it, the padding 6' has a hard, outer shell 54' that is substantially flat or at least flatter than the shell 54 of FIG. 24. Additionally, casing 20 of FIGS. 35-37 is segmented at 34 (see FIGS. 36 and 37) to create multiple pouches 50. Each pouch 50 is preferably attached to the shell 54' as, for example, using rivets, hook and loop fasteners, or snaps. All of the pouches 50 are preferably underfilled as in FIG. 36 but could be gravity filled, overfilled, or a mix of the various degrees of filling. For example as shown in FIG. 37, the top pouch 50 could be underfilled, the middle pouch 50 gravity filled, and the bottom pouch 50 overfilled.

FIGS. 38-40 illustrate further modified padding 6" in which a pontoon-shaped, inner layer 86 (see FIG. 39) of beaded casings 20' with an interconnecting piece of material 88 is used with an overlying layer 90 of interconnected casings 20. The spaced-apart, pontoon casings 20' of layer 86 can be overfilled, gravity filled, or underfilled with beads. The layers 86 and 90 as shown are preferably attached at 60 (e.g., by stitching or rivets) to the hard, outer shell 54' with the respective casings 20' and 20 of the layers 86 and 90 staggered or nested relative to each other. In this manner, the layers 86 and 90 assume a relatively low profile. More importantly, the staggering positions the central pouch or casing 20 of layer 90 against the piece of material 88 extending between the pair of pontoon casings 20' of layer 86. The central casing 20 of layer 90 positioned against the connecting material 88 then essentially forms a triangle with the pair of pontoon casings 20' (see FIG. 38). Consequently, in use when a force 9 is applied as in FIG. 38, the force 9 will press the central casing 20 of the outer layer 90 against the piece of material 88 connecting the pontoon casings 20'. This in turn will transfer and spread out (dissipate) the force to the pontoon casings 20' somewhat in the manner of FIG. 29. As best seen in FIG. 40, the result of the layering and pontoon structure is that essentially all of the beaded casings 20' and 20 of both layers 86 and 90 are flattened and compressed against the athlete's body 15. To improve the flattening and increase the contact, surface area against the athlete's body 15, the pontoon casings 20' are preferably smaller than the casings 20 of the outer layer 90. The force or impact 9 is then not only greatly dissipated but also the transfer time through the pad 6" is significantly increased (e.g., by 1-2 milliseconds). The material 88 is preferably elastic to better accommodate the movement and flattening of the casings 20' and 20 of both layers 86 and 90 against the athlete's body 15. As shown, the upper and lower casings 20 of the outer layer 90 of FIG. 38 are also suspended in a similar manner by the pieces 88' of elastic material extending respectively between each of the attachments 60 and one of the pontoon casings 20'. In a similar but less effective way, forces applied to these upper and lower casings 20 of layer 90 are also transferred and dissipated through the immediately adjacent pontoon casing 20'.

FIGS. 41 and 42 show a doughnut-shaped pad 92. The pad 92 is segmented at 34 wherein the filling degree of the various, beaded pouches 50 could be varied as desired in a manner similar to the padding 6' of FIG. 37. In one application of the pad 92 of FIG. 41 to protect, for example, the

14

top of a shoulder and clavicle, the central pouch 50 might be underfilled or at least filled to a lesser degree than the surrounding pouches 50 (which could be overfilled, gravity filled, or underfilled). The pad 92 of FIGS. 41-42 as well as the one of FIGS. 43-44 discussed below could be used with or without a hard, covering shell 54.

The pad 96 of FIG. 43 has an initially gravity filled or underfilled casing 20 attached to a stretchable band 98 such as would be applicable for use as an elbow, knee, or arm pad. In use, the stretchable, elastic band 98 will actually distort and constrict or reduce the volume of the casing 20 (compare FIGS. 43 and 44). The initially gravity filled or underfilled casing 20 of FIG. 43 will then assume the overfilled condition of the first set of protective padding of FIGS. 1-23 and act in the same manner. FIGS. 43 and 44 thus illustrate a method for creating an overfilled pad from an initially underfilled or gravity filled one. In doing so, the initially underfilled or gravity filled casing 20 is pressed against (stretched about) the user's body (i.e., arm 17 in FIG. 44) until the volume of the casing 20 is distorted or reduced to create an overfilled condition. The inelastic casing 20 is then under tension and substantially all of the beads are in compression. If the casing material is elastic, then the distortion preferably stretches the casing material to its elastic limit. Either way, the mere placing of the pad 96 on the athlete's arm 17 overfills the casing 20 and places it in condition to receive a blow in the manner of FIGS. 9-11. The pad 96 is preferably not used in combination with a hard, outer shell 54 but could be if desired.

In the embodiment of FIGS. 45-46, the beads 22 (whether a blend of beads 66, 68, and 70 or not) are fused together wherein the pad itself assumes a predetermined shape. The beads are preferably a mix so that the characteristics of the overall pad, including softness and transfer time (attenuation) of the force through it, can be varied as desired. The fusing can be done, for example, by lightly steaming or gluing the beads. The shaping could be done by simply fusing the beads within a mold to create the desired shape or the desired shape could be achieved by first fusing the beads into boards or other bulk forms that were then cut to the desired shape. The fused beads could be used with or without an outer casing 20. When an outer casing 20 is used, it would preferably be attached about the beads either prior to or during the fusing process but could be done afterward. The fit of the casing 20 about the beads could be loose or snug but preferably would place the casing 20 in tension as, for example, by a shrink-wrapping process (e.g., heat up the polypropylene casing 20). This would also place the beads in a slight compression. The resulting pad 12' could then be used, for example, in the helmet 5 of FIG. 1 and removably attached in place to the hard shell of the helmet 5 using hook and loop fasteners (e.g., Velcro) 100 or snaps or more permanently attached with rivets if desired. The pad 12' could be nominally fashioned in progressive sizes to fit the contours of the athlete's head 19 or custom fused and shaped to the particular athlete exact shape. The casing 20 in this regard helps the pad 12' to maintain its integrity, particularly if the casing 20 is shrink-wrapped in place or otherwise attached to the beads (e.g., by glue). Further, should the pad 12' become fractured, the casing 20 helps to hold the pieces together. The casing 20 is preferably a very porous and breathable mesh and the beads are preferably made of lightweight, closed-cell foam. Even though adjacent, abutting portions of the fused beads are joined to each other, there still is a significant amount of interstitial spaces between the beads, which interstitial spaces and resulting high porosity and breathability preferably are substantially

15

uniformly distributed throughout the entire pad 12'. The result is then a waterproof yet highly porous and breathable pad 12' that can be pre-shaped as desired. Like all the other, preferred pads and padding of the present invention, the pad 12' itself, does not absorb water or odors, is relatively cool to wear, and can be easily washed. In another embodiment, the waterproof beads 22 of the pad 12' of FIGS. 45-46 are made of substantially inelastic or crushable material (e.g., closed-cell polystyrene foam) and are preferably first subjected to a corona treatment in an inert gas atmosphere (e.g., a noble gas such as argon) to raise the surface energy of the beads 22 and then fused together (e.g., with an adhesive such as a water-based urethane or neoprene).

In the embodiment of FIGS. 47-48, a modified casing 102 is used which has a substantially waterproof and airtight upper portion 104 and a flexible, porous, breathable, lower portion 30 as in prior embodiments. Separating the two portions is an intermediate portion or layer 106 of the same material as portion 104. The upper half or compartment formed by portions 104 and 106 of the casing 102 is filled with a layer of open-celled foam 108 (e.g., urethane) and the lower half or compartment bounded by portions 30 and 106 is filled as in the prior embodiments with closed-cell, foam beads 22 (e.g., polypropylene). The boundaries at 36 of the portions 104, 106, and 30 are preferably sewn together at 110. In use when a blow or force 9 is applied as in FIG. 48, the upper half of the casing 102 is depressed under the force of the blow 9 to compress the open-celled foam 108 as well as the beads 22 in the lower half of the casing 20. The air from the open-cell foam 108 in the upper half of the casing 102 is expelled at 112 primarily through the holes about the stitches 110. Depending upon the characteristics of the sewing (e.g., spacing or number of stitches 110 per inch, the size of the stitch holes relative to the size of the stitches 110 themselves, the degree the pad is heated to vary the size of the stitch holes, the porosity of the material of the stitches 110, and the degree to which portions 104 and 106 are pressed or sealed together between the stitches 110), the rate

16

of the escaping air 112 can be varied as desired. This in turn will give the overall pad varying degrees of softness and transfer time. The material of portion 104 in this regard is preferably waterproof and airtight (e.g., treated nylon) but could be waterproof and slightly porous to air if desired. The degree of air porosity through the material of 104 could then be varied to further modify the rate of the escaping air without adversely affecting the waterproofness of the upper compartment. The foam 108 in the upper half within portion 104 is preferably slightly compressed in the initial condition of FIG. 48. The beads in the lower half within portion 30 in FIG. 48 can be a mix if desired and this lower half of the casing 102 can be initially overfilled, gravity filled, or underfilled depending upon the particular application. In the preferred embodiment, the upper and lower halves or compartments of the casing 102 initially are filled to have substantially semicircular cross sections as illustrated in FIG. 48. As with the other embodiments, the pad of FIGS. 47-48 could be used with a hard, outer shell if desired.

We claim:

1. A porous, breathable pad for use as protective padding by a person to absorb the force of an impact and to protect the user from injury while allowing liquids and air to freely pass through the pad, said pad having a plurality of discrete, substantially solid beads of substantially inelastic and waterproof, closed-cell foam wherein some outer portions of adjacent beads abut one another and other outer portions of said adjacent beads are spaced from each other to create interstitial spaces, at least some of said adjacent beads being fused together at the abutting, outer portions thereof.

2. The pad of claim 1 wherein substantially all of said adjacent beads are fused together at the abutting, outer portions thereof.

3. The pad of claim 1 wherein said fused beads form a predetermined shape.

4. The pad of claim 1 wherein said interstitial spaces are substantially uniformly distributed throughout the pad.

* * * * *



US005394786A

United States Patent [19]

Gettle et al.

[11] Patent Number: 5,394,786

[45] Date of Patent: * Mar. 7, 1995

[54] ACOUSTIC/SHOCK WAVE ATTENUATING ASSEMBLY

5,225,622 7/1993 Gettle et al. 86/50

[75] Inventors: Guy L. Gettle, Walnut Creek, Calif.;
Vincent H. Homer, Jr., Jeddeh, Saudi
Arabia[73] Assignee: Suppression Systems Engineering
Corp., Santa Clara, Calif.[*] Notice: The portion of the term of this patent
subsequent to Jun. 6, 2010 has been
disclaimed.

[21] Appl. No.: 81,998

[22] Filed: Jun. 30, 1993

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 834,411, Feb. 12, 1992,
Pat. No. 5,225,622, which is a continuation-in-part of
Ser. No. 541,030, Jun. 19, 1990, abandoned.[51] Int. Cl.⁶ F42B 33/00[52] U.S. Cl. 86/50; 367/191;
181/286; 181/0.5; 89/36.02; 102/303[58] Field of Search 86/50; 367/191;
181/286, 0.5; 89/36.02; 102/303

[56] References Cited

U.S. PATENT DOCUMENTS

4,454,798	6/1984	Shea et al.	181/223
4,543,872	10/1985	Graham et al.	86/50
4,589,341	5/1986	Clark et al.	102/303
4,836,939	6/1989	Hendrickson	252/3
4,903,573	2/1990	Browne et al.	86/50
4,964,329	10/1990	Moxon et al.	86/50

OTHER PUBLICATIONS

Walters, W. P., *Fundamentals of Shaped-Charges*, John
Wiley & Sons, Inc. (1989), pp. 13-14.Fricke, J., "Aerogels", *Scientific American*, vol. 258,
No. 5, May 1988, pp. 92-97.

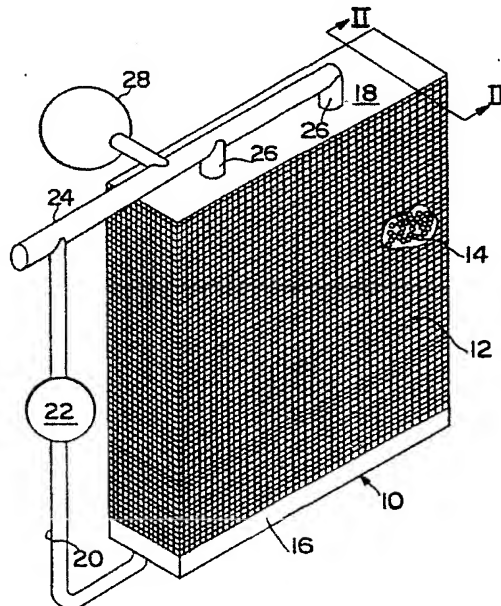
Primary Examiner—J. Woodrow Eldred

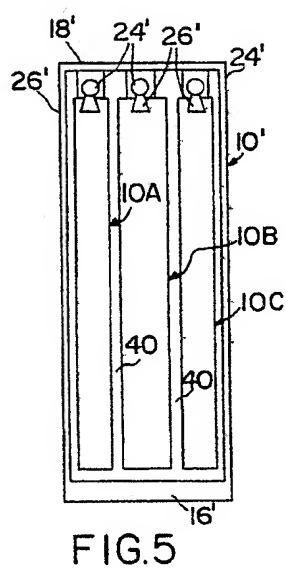
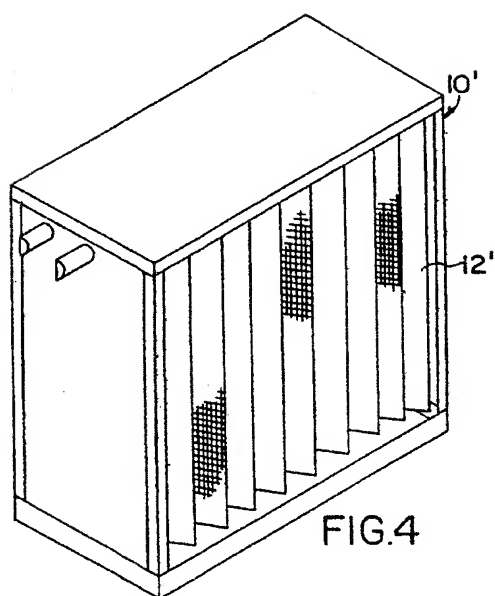
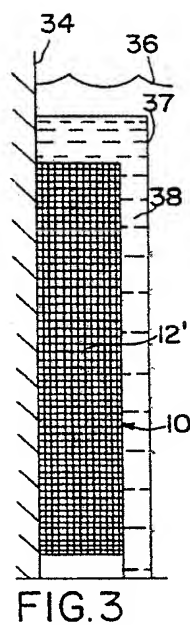
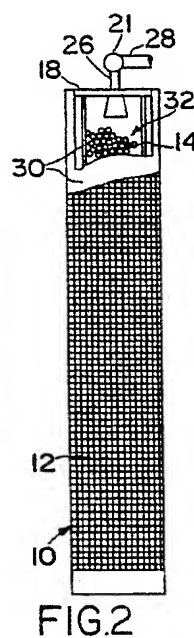
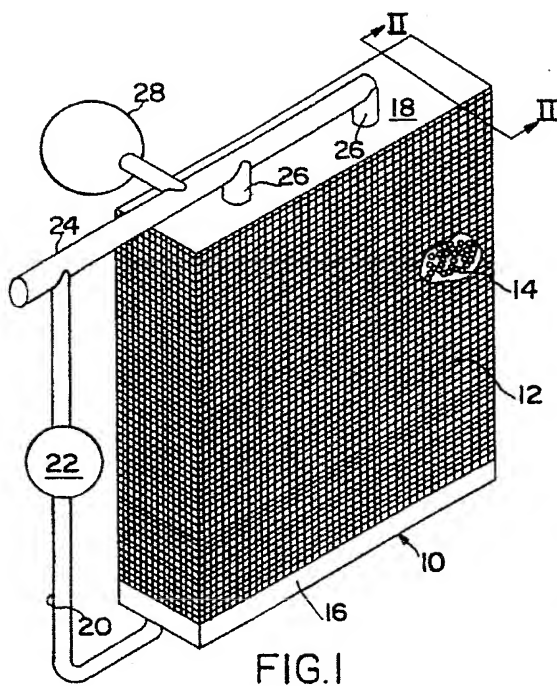
Attorney, Agent, or Firm—John A. Bucher

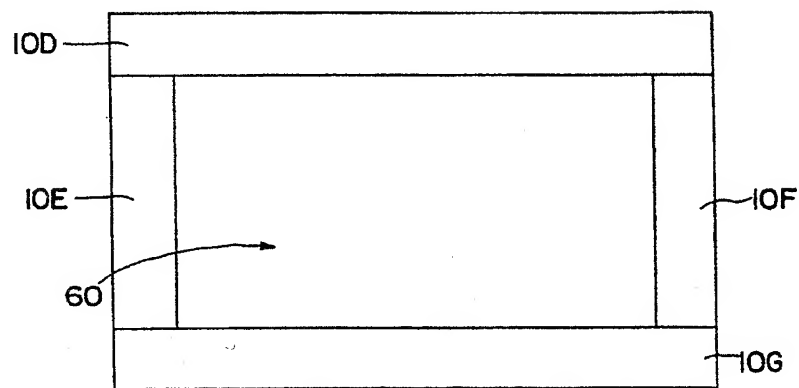
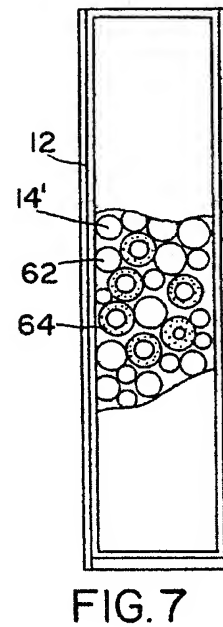
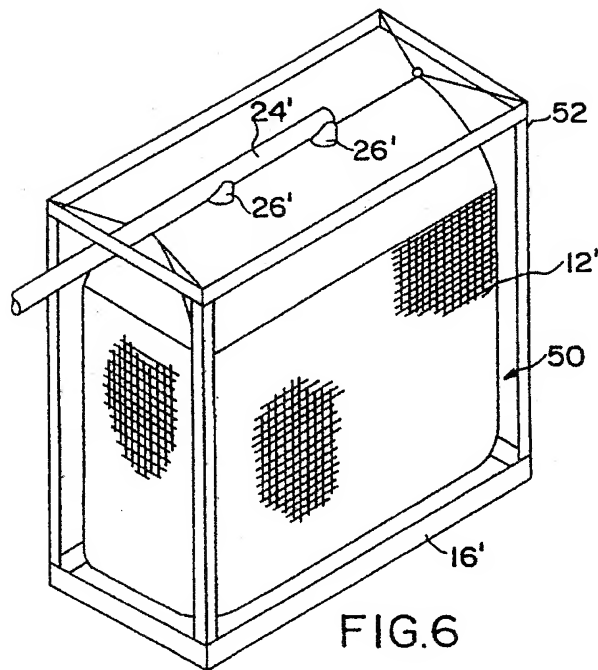
[57] ABSTRACT

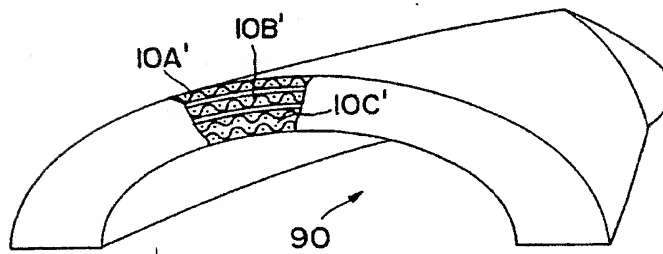
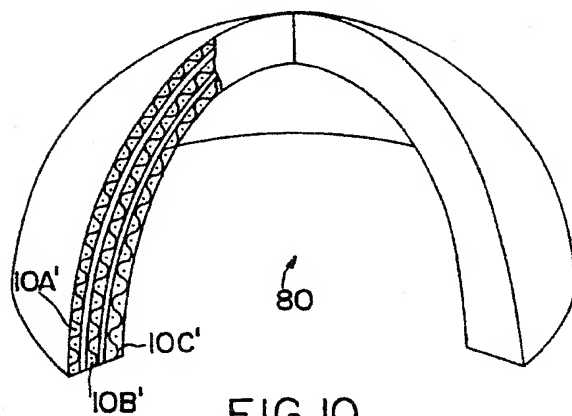
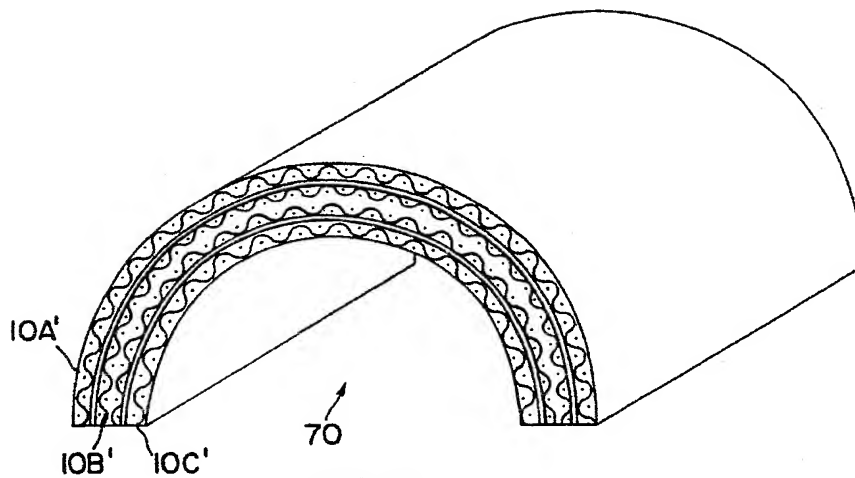
An acoustic/shock wave attenuating assembly comprised of porous screens forms an enclosure filled with a suitable pressure wave attenuating medium or material having fluid characteristics. This basic configuration can be suspended or held in place by a rigid structure. When the pressure attenuating medium is a liquid, the attenuating assembly is provided with a lining for containment. Multiple attenuating assemblies can be employed, with adjacent attenuating assemblies separated by a small gap. The pressure attenuating medium may be a liquid, a gas emulsion, an aqueous foam, or a gel (with or without entrained gas). Alternatively, solid particulates having bulk mechanical properties of a fluid may be employed as the pressure wave attenuating medium and may have an adhesive or the like resisting relative movement between particulates to simulate viscous effects. Elements of the assembly may incorporate materials which absorb thermal energy through endothermic chemical reactions, such as intumescent materials, to enhance the pressure attenuating effect.

31 Claims, 6 Drawing Sheets









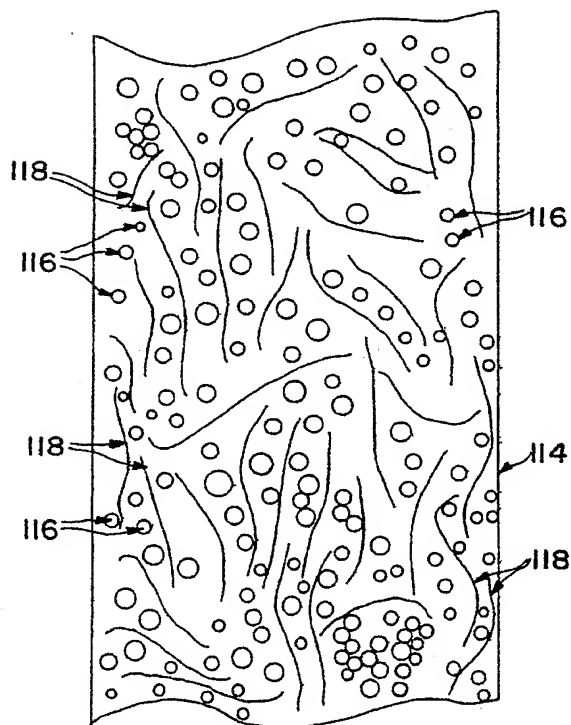


FIG. 12

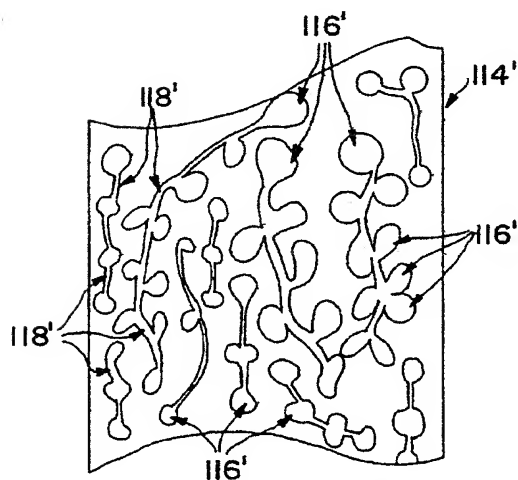


FIG. 13

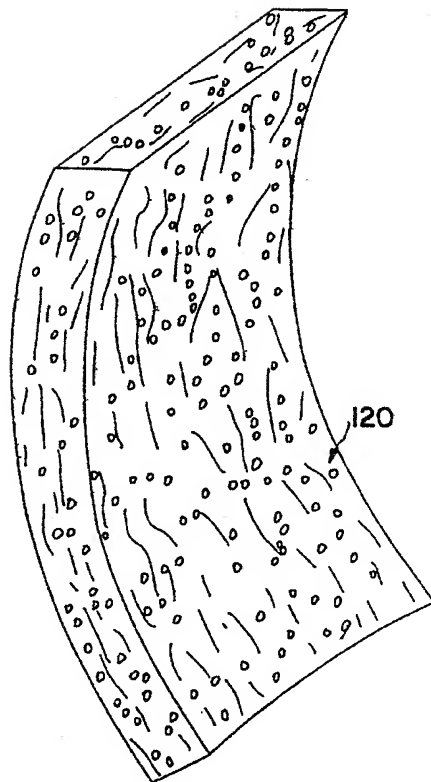


FIG. 14

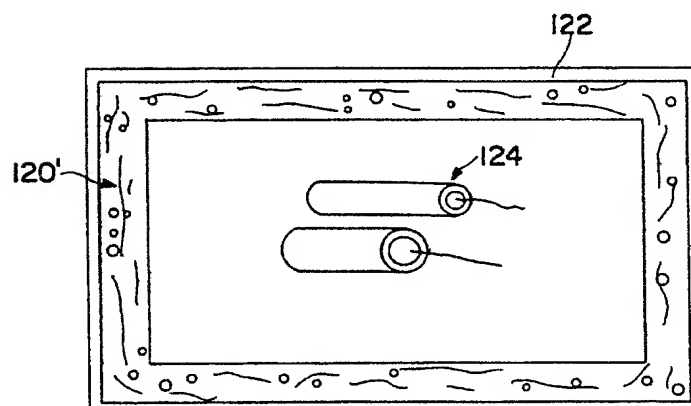


FIG. 15

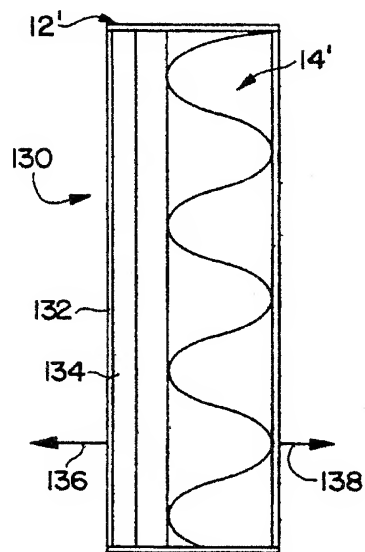


FIG. 16

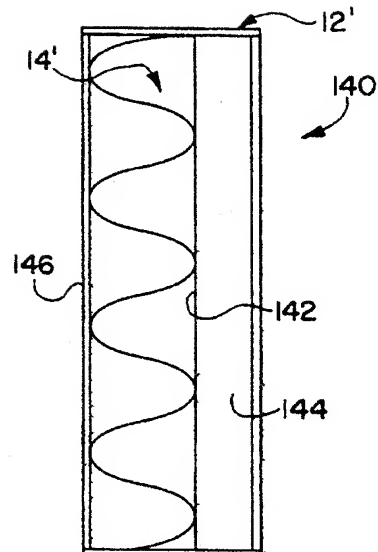


FIG. 17

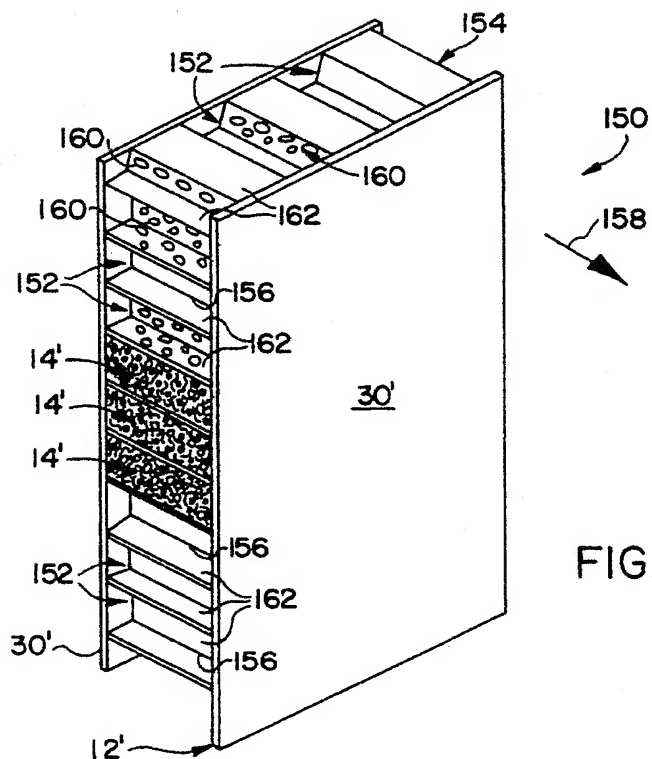


FIG. 18

ACOUSTIC/SHOCK WAVE ATTENUATING ASSEMBLY

This is a continuation-in-part of application Ser. No. 07/834,411, filed Feb. 12, 1992, and issuing on Jul. 6, 1993, as U.S. Pat. No. 5,225,622, that application in turn being a continuation-in-part of application Ser. No. 07/541,030, filed Jun. 19, 1990, now abandoned.

FIELD OF THE INVENTION

This invention relates to pressure wave phenomena (acoustic and shock waves) and more specifically to an assembly for providing attenuation of pressure waves traveling generally at or above the speed of sound in ambient conditions in order to mitigate undesirable effects of these waves (including fragments and thermal energy release).

BACKGROUND OF THE INVENTION

Acoustic and shock waves are traveling pressure fluctuations which cause local compression of the material through which they move. Acoustic waves cause disturbances whose gradients, or rates of displacement are small—on the scale of the displacement itself. Acoustic waves travel at a speed determined by and characteristic of a given medium; thus, one must speak of the speed of sound, or acoustic speed in that medium. An acoustic wave regardless of its frequency (pitch) or amplitude (loudness), will always travel at the same speed in a given substance.

Shock waves are distinguished from acoustic waves in two key respects. First, shock waves travel faster than the speed of sound in any medium. Secondly, local displacements of atoms or molecules comprising a medium caused by shock waves are much larger than for acoustic waves. Together, these two factors produce gradients or rates of their displacement much larger than the local fluctuations themselves.

Energy is required to produce pressure waves. This is related to the equation that states that energy equals force multiplied by the displacement caused by the force. Once the driving source ceases to produce pressure disturbances, the waves decay. Attenuation involves acceleration of the natural damping process, which therefore means removing energy from pressure waves.

All matter through which pressure waves travel naturally attenuates these waves by virtue of their inherent mass. Materials possess different acoustic attenuating properties, strongly affected by density and by the presence or absence of phase boundaries and structural discontinuities. Porous solid materials, thus, are better attenuators of sound waves than perfect crystalline solids. Gases are inherently poor pressure wave attenuators.

All types of pressure waves can be reflected and diffracted by liquid and gas media. They can also be deflected or, more generally, scattered and dispersed by phase boundaries, such as liquid droplets or solid particulates suspended in air. These deflections serve to increase the distance which the wave travels. Scattering and dispersion thus produce more attenuation because they cause the transmitting pressure waves to displace more mass by virtue of the longer path. Such deflections also reduce, or may altogether eliminate the pressure waves originally traveling in a specific direction.

Acoustic Wave Attenuation

Documented efforts to reduce noise (attenuate acoustic waves) in enclosed spaces extend to the early nineteenth century. Virtually all acoustic wave attenuation concepts have been based upon layers of solid materials with significant sound absorbing properties serving as linings, coatings, or loosely-packed fibrous or granular fillers between solid layers. These sound-absorptive layers have been applied to or incorporated within structural walls, floors, ceilings, and other types of panels and partitions when acoustic attenuation is required. Several dozen patents have been granted in the United States alone which fall into this category.

In 1910, Mallock introduced the idea of using aqueous foams for noise suppression, and conducted experimental evaluation of foams in this role. See Mallock, A., "The damping of sound by frothy liquids", *Proc. Royal Soc. A84*; pp. 391-5, 1910. Aqueous foams are agglomerations of bubbles, with the gas phase within each bubble completely separated from that in adjacent bubbles by aqueous liquid film comprising the bubble walls. During the years following Mallock's research, aqueous foams became widely used for fire suppression, in numerous chemical processes, and for mineral ore separation.

Not until the 1960's did interest renew in using aqueous foams for pressure wave attenuation. Research from that time and continuing to the present extended to their use for suppressing jet engine noise and acoustic disturbances arising from artillery muzzle blast, ordnance disposal, and "sonic boom" created by supersonic aircraft flight. It was during this time that researchers discovered that aqueous foams dramatically attenuate impinging shock waves.

Shock Wave Attenuation

Much more energy is required to produce shock waves compared to acoustic disturbances, which makes their attenuation more difficult. Shock waves decay to form acoustic waves when the source of the shock wave is removed or suppressed.

When traveling through gases, shock waves produce increases in pressure (often referred to as "overpressure") and temperature; they also accelerate gas molecules and entrained particulates in the direction of shock wave travel. Shock waves produced by combustion processes, such as explosions and deflagrations, release substantial amounts of thermal and radiant energy as well. For all shock waves, the shock wave speed, overpressure, and temperature increase they induce in the local medium are mathematically linked. Attenuation of shock waves is thus achieved through directly suppressing one of these three parameters; if temperature is reduced, the overpressure and shock speed are accordingly reduced, for example.

Mitigation of shock wave parameters has required different approaches than those used for acoustic wave attenuation because of their relatively large impulse and pressure magnitude. Mechanical mitigation methods can be applied in many situations where barriers or confinement are allowable. When shock waves are produced by explosions or deflagrations, chemical means as well can often be used for suppression. None of the structures or materials described in existing patents or in technical literature similar to the types of solid sandwich configurations discussed above for noise suppression can provide significant attenuation of shock waves.

Two types of structures or mechanical arrangements have been employed in reducing shock wave effects: solid barriers (including blast mats) and mechanical venting. Solid barriers and blast mats have been used to deflect incident shock waves or remove energy from incident waves through momentum transfer (to the high-inertia mats and barriers), and to provide protection from fragments and thermal effects. Mechanical venting has been employed to keep internal pressure below the level which would cause structural failure for explosions in confined spaces.

Solid barriers for shock wave containment or protection suffer from several shortcomings. Where protection of large areas from powerful shock effects is necessary, concrete or earthen barriers must be employed. These structures must be massive and are thus inherently immobile and expensive and time consuming to erect. They cannot, therefore, be used in the majority of applications where explosion hazards are present: marine transport of liquid and liquefied hydrocarbons, petrochemical storage and processing facilities, aboard warships and munition-carrying vessels, or at hastily established munitions transshipment points (which are common in military operations, for example). They cannot be used within buildings or otherwise serve as partitions in structures.

Similarly, large numbers of bulky and heavy blast mats are required for blast overpressure exceeding a 1-meter scaled distance (the equivalent blast wave intensity of a 1-kilogram TNT detonation at a distance of 1 meter). When not being used, these mats must be stored. Aboard ships, space is often critically limited, thus bulky items which provide no essential or alternate use cannot be justified. Furthermore, blast mats can at best provide only limited mitigation of blast effects in confined spaces and provide little acoustic damping. Their bulk, weight, and limited utility in confined spaces rule out their employment aboard aircraft. Blast mats cannot be easily or quickly moved from storage to locations where needed for blast wave attenuation due to their bulk and weight.

Mechanical venting is widely employed for mitigating blast overpressure in containment structures (grain silos, explosive material handling rooms, etc.) These vents normally constitute part of the containment wall. Besides reliability and response time problems, venting requires facilities to be designed such that overpressure release will not endanger personnel or nearby structures. Venting cannot be employed where hazardous materials may be released. Venting is also unacceptable aboard ships, where openings to the sea and release of smoke and overpressure within the vessel are dangerous. Mechanical venting cannot be used for noise attenuation.

Chemical agents suppress shock waves by extinguishing or interrupting the combustion process which generates them (along with their thermal effects). Such agents include carbon dioxide and halogenated carbon compounds ("halons"), which may either be gaseous or liquid initially at the time of application, and dry powders, most of which are salts of ammonium or alkali metals such as sodium and potassium.

Gaseous combustion-extinguishing agents are generally effective in confined spaces. A number of constraints limit their utility, however. No gaseous agent is effective in outdoor or well-ventilated areas. Within a confined space, effectiveness of gaseous agents is rapidly lost as these agents quickly escape through leaks

and penetrations (including those caused by projectiles or weapons fragments which generate the need for gas agent release). All of the gas and liquid (which become gaseous in use) chemicals currently available for fire and explosion suppression have toxic effects upon humans at the concentrations required to be effective.

The most effective and least toxic gaseous agents are halogenated carbon compounds. However, these substances are quickly and irreversibly broken down while performing their combustion-inhibiting function. Furthermore, these agents are being withdrawn from use by international government agreements due to their profoundly adverse impacts upon upper-atmospheric ozone.

Other considerations limit the capabilities of gas fire-extinguishing agents. They cannot provide significant acoustic attenuation in and of themselves. Furthermore, gases cannot provide cooling or quenching of the area surrounding a fire or explosion due to their inherently low heat capacities, which enables hot surfaces to reignite combustible materials. Gas supplies must be adequate for extinguishment and be capable of reaching all spaces within a compartment, otherwise they have no effect. Gaseous explosion suppression systems are totally dependent upon sensors to initiate release (within 100 milliseconds), which has proven to be a problem because of false-alarm activation or failure to activate, due to the vulnerability of their sensors to dirt and contaminants. Sensors also require maintenance to ensure minimum reliability.

Powdered fire fighting agents (chemical extinguishants) can be effectively used in both confined and unconfined areas for fire suppression—and by virtue of their dissociation and combustion interrupting tendency—can suppress some deflagrations which could produce shock waves. Again, however, they cannot provide acoustic attenuation or fragment or missile-stopping capability. Furthermore, they require large quantities of agent (with consequent bulk and weight) to provide significant extinguishing capability. Flooding a space with powdered agents is blinding to personnel present during emergency operations.

Pressure Wave Attenuation Using Aqueous Foams

Aqueous foams have been proven to be capable of providing more pressure wave attenuation than any other medium on a mass basis. As noted above, initial research into the use of aqueous foams for pressure wave damping was entirely devoted to noise abatement. Subsequent research revealed, that—unlike any material used in acoustic attenuation structures developed to date—aqueous foams provide shock wave attenuation, regardless of the origin of the shock.

All applications to date of aqueous foams for pressure wave attenuation have been in two basic forms: unconfined deluge or massive foam flooding and employment of solid confining walls in which aqueous foam is placed. Massive deluge or high-capacity foam generation systems have been used for perimeter security and for flooding of buildings to provide explosion protection from bombs. Aqueous foam-filled containers have also been used for safe removal and disposal of explosives. Variants of the foam-filled container concept have been developed as noise-attenuation devices ("silencers") for the muzzles of firearms and large naval guns.

In spite of their successful application to date, current methods and systems for using aqueous foams in pres-

sure attenuating roles are inefficient and unnecessarily bulky. Furthermore, such methods and systems prevent the full capabilities offered by aqueous foams from being realized because they require that the foam attenuate the incident shock or acoustic wave without mechanical augmentation or assistance. Solid walls utilized in current approaches are used only for fluid confinement and stopping fragments. Such usage requires much larger volumes of foam (foam agent and water) along with larger pumps and foam generating equipment than are necessary to provide a specified level of pressure wave attenuation.

Comparisons Between Solid and Aqueous Foams

Acoustic attenuation by both types of materials are comparable due to the fact that both rely upon scattering and dispersion of sound waves at bubble/cell walls. Solid foams are more compact, aqueous foams are more efficient on a mass basis. Major differences appear in regard to shock wave attenuation, however.

Solid materials, including solid foams, used as rigid panels are unable to attenuate shock waves because of two factors: the large amplitude of the displacements of atoms or molecules during shock wave propagation and the overpressure created in the surrounding fluid. Shock waves propagating through aqueous foams create turbulent flow fields, which have been shown to dissipate substantial amounts of energy, particularly when reflected waves travel through the turbulent medium. See Khosla, A. "A study in shock wave attenuation", Ph.D. thesis, pp. 229-30, U. of Calgary, 1974. Turbulent flow fields cannot be generated within solid materials.

The relatively large displacement of the liquid mass contained within aqueous foam bubbles is resisted by surface tension and viscous forces, removing considerable shock wave energy as well. Again, such displacements cannot occur within solids, even elastomeric foams. Most shock wave energy encountering solid layers of any kind—including solid foams—is reflected, which produces overpressures exceeding the incident level. Furthermore, shock wave overpressures can knock down solid panels and walls without expending much energy.

Significant dissipation of shock wave energy can be accomplished with solid materials, according to the present invention as discussed further below, when the solid materials are used as loosely packed beads, in which form they are capable of relative displacement in the nature of a fluid. In such a form, the beads act similarly to bubbles in an aqueous foam. Specifically, transmitting shock waves are scattered and dispersed at the bead surfaces, and the displacement of the bead mass absorbs substantial energy. Substantially more shock wave energy can be absorbed when the beads are made to resist displacement to a limited extent (below the degree where the bead mass would act more as a rigid panel than a fluid). This can be accomplished by means of an adhesive surface coating or by a surface texture which promotes friction or adherence.

Experimental work has shown that volcanic foam glass (vermiculite) beads have been able to attenuate shock waves originating from small explosives comparable to the extent achieved by some aqueous foams. Vermiculite, however, provides less acoustic attenuation than solid organic foam materials such as natural rubber and polyurethane, which are normally used in this role. Furthermore, neither vermiculite nor any

solid material used to date for acoustic attenuation has combustion extinguishing properties in and of itself; indeed, most organic solid foam materials are serious contributors to fire and toxic smoke generation.

Aqueous foams have additional mechanisms for dissipating shock energy which no solid bead material can provide: elastic bubble walls which absorb energy when they are deformed or ruptured, by uniquely and dramatically slowing shock waves propagating through, and—in the case of stronger shock waves—by causing these shock waves to separate into two separate waves, which are then more easily attenuated.

The references discussed above are incorporated herein as though set forth in their entirety, to facilitate understanding of the present invention, particularly in connection with the function and materials of aqueous foams.

SUMMARY OF THE INVENTION

In view of the shortcomings for existing apparatus and assemblies to attenuate acoustic and/or shock waves as noted above, there has been found to remain a need for an improved assembly for more effectively attenuating acoustic and/or shock waves. The present invention accordingly provides a means for attenuating substantially all types of pressure waves, existing as either an acoustic or shock wave, in generally all gaseous environments, particularly in ambient atmospheric conditions. More specifically, the invention provides a means or assembly for substantial suppression or attenuation of blast effects from either proximate or remote explosions as one of the more severe examples of pressure wave or acoustic/shock wave conditions effectively dealt with by the invention.

The term "acoustic level pressure condition" is employed herein to include both acoustic waves at the acoustic speed of a selected medium and/or shock waves exceeding the acoustic speed of a selected medium. Accordingly, that term is employed as a replacement for either or both conditions of acoustic waves and/or shock waves.

As discussed in greater detail elsewhere, the invention contemplates sonic/shock wave pressure conditions preferably traveling at or above the acoustic speed for a given medium. However, it will be apparent that the invention is also effective for pressure conditions generally approaching acoustic speeds in a given medium and thus exhibiting pressure characteristics to be desirably attenuated in the same manner as acoustic/shock wave configurations.

In view of the above summary, the invention has a number of objects and advantages set forth as follows:

- (a) to provide pressure wave attenuation capabilities in both confined spaces and unconfined areas;
- (b) to provide attenuation of all acoustic frequencies regardless of orientation with respect to the source;
- (c) to provide shock wave attenuation in confined spaces without requiring the space to be completely filled by aqueous foam or any other agent or medium;
- (d) to provide attenuation of shock waves for both proximate and remote explosions;
- (e) to provide a specified level of pressure wave attenuation in less volume and with lower weight than is possible through any other existing means;
- (f) to provide shock wave attenuation in confined spaces without requiring the confining walls to be gas-tight (free from leaks or penetrations);

(g) to provide pressure wave attenuation with a mechanical configuration which can be quickly stowed or removed to provide passageway or space when the system is not in use;

(h) to provide a pressure wave attenuation structure to which other means of augmenting specific attenuating capabilities or to provide additional capabilities can be applied or installed within (such as adding insulation to protect the system from fire or radiation, providing intumescent coatings to provide additional thermal energy absorption from proximate explosions, or to include chemical fire-suppressing power or gaseous agents within); and

(i) to provide explosion protection using the same agent as employed for fire fighting (aqueous foam fire suppressants).

More specifically, the present invention provides an acoustic/shock wave attenuating assembly formed by a flowable attenuating medium exhibiting aqueous foam characteristics and a confinement means for containing and supporting the flowable attenuating medium, the confinement means being porous with respect to the acoustic/shock wave for allowing the shock wave to penetrate the flowable attenuating medium. Porosity of the confinement means is more specifically characterized as macroscopic or microscopic openings allowing the shock wave to pass therethrough but, at the same time, absorbing considerable energy from the shock wave and creating turbulent zones or large numbers of miniature shock waves as energy from the shock wave passes into the flowable attenuating medium. With such porous material being preferably arranged on opposite sides of the attenuating medium, similar energy absorbing conditions occur as the shock wave penetrates and passes through both sides of the confinement means. In addition, substantial energy from the shock wave is absorbed by the flowable attenuating medium, particularly because of its containment and restriction by the confinement means.

Preferably, the flowable attenuating medium is an aqueous foam known to have substantial energy absorbing capabilities from the prior art as discussed above. However, the flowable attenuating medium may also be formed, for example, from solid particulate material preferably having bulk mechanical properties and flow properties of a fluid, the solid particulates also preferably comprising means for resisting relative displacement of the particulates in order to better simulate characteristics of an aqueous foam. In this regard, the term "flow properties of a fluid" and more specifically the term "mechanical properties and flow properties of a fluid" refer to the ability of the attenuating medium to act in the nature of a liquid mass to resist relative displacement by surface tension and viscous forces and the ability to substantially scatter and disperse pressure conditions transmitting therethrough by virtue of multitudinous curved surfaces dividing gaseous and solid or liquid or solid phases, and enabling the generation of turbulent flow fields by transmitting pressure conditions. More briefly, these terms may be taken as referring to the ability to resist applied shear forces in the nature of fluid viscosity. Finally, the above terms are also intended to refer to a tendency of the flowable attenuating medium to assume the shape of the confinement means while at the same time resisting applied shear forces in the nature of viscosity.

Numerous configurations are possible for the attenuating assembly of the invention. Preferably, the confine-

ment means provides generally parallel side portions forming a panel in combination with the flowable attenuating medium supported therebetween for intercepting the acoustic/shock wave. More preferably, both side portions of the confinement means are porous in order to achieve maximum attenuation in the manner summarized above. It is even further contemplated that a plurality of such panel formations can be arranged with intervening gaps whereby the acoustic/shock wave may be effectively caused to successively penetrate the plurality of panel formations and intervening gaps in order to even more effectively attenuate the acoustic/shock wave.

A further possible configuration of the invention provides for placing the acoustic/shock wave attenuating panel combination between a structure and a surrounding liquid medium such as sea water for the purpose of protecting the structure from shock waves or other pressure wave phenomena arising from underwater explosions or seismic activity. In this application, an acoustic/shock wave attenuating assembly of one of the above mentioned configurations employs a non-porous membrane or rigid shell confinement means to isolate the surrounding liquid from a liquid transmitting medium emplaced between the confinement means and the acoustic/shock wave attenuating assembly. Preferably the flowable attenuating medium is an aqueous foam and the transmitting liquid medium being a homogeneous liquid without macroscopic gas bubbles or solid particulates in suspension.

It is also contemplated that the panel combination may be shaped to form a generally enclosed chamber. With both side portions of the confinement means being porous to the acoustic/shock wave, such a configuration is effective to attenuate the acoustic/shock wave passing in either direction through the panels.

It is yet another object of the invention to provide such a flowable attenuating medium in solid form, the attenuating medium being formed by solid particulates which may be hollow or otherwise include a gaseous phase, the particulates preferably being macroscopic and even more preferably have a dimension of at least about one millimeter.

It is a related object of the invention to provide such a solid attenuating medium wherein solid particulates are supported and more preferably also confined by a filamentary material forming a matrix. In such a configuration, the filamentary material preferably has mechanical integrity for providing confinement of the solid particulates in the matrix of filamentary material while allowing the solid particulates to be relatively displaced by interaction with pressure conditions so that the panel is capable of scattering and dispersing the pressure conditions passing therethrough. In such a configuration, the attenuating medium or panel further enables formation of turbulent flow fields from the pressure conditions.

Within such a configuration, the attenuating medium may be in the form of a flexible attenuating panel and may further comprise means interacting with the solid particulates and filamentary material in order to increase resistance of the solid particulates to relative displacement by the pressure conditions in addition to resistance attributable to inertia forces.

It is a still further object of the invention to provide a flowable attenuating medium for the present invention in the form of an aerogel, a very light weight material described in greater detail below.

It is also a further object of the invention to provide the attenuating medium and related components for protective applications, particularly in connection with ammunitions or devices of a type generally referred to as shaped-charge or hollow-charge devices, as described in greater detail below.

It is a related object of the invention to also employ the attenuating medium and related components of the invention for protecting explosive charges or devices themselves from interaction or detonation, this phenomenon being commonly referred to as "sympathetic detonation", "fratricide", "propagation" or "chain reaction", as also described in greater detail below.

It is yet a further object of the invention to employ the attenuating medium and associated components of the invention to provide a liner for containers, either to protect the contents of the container from external blasts or to protect the exterior of the container from blasts within the container. Accordingly, the invention particularly contemplates use in connection with air cargo containers and the like.

It is also a further object of the invention to employ a shield of a frangible material in combination with the attenuating medium for protecting against weather and the like while still permitting the desired function of the attenuating medium as also described in greater detail below.

It is another object of the invention to employ the attenuating medium in combination with honeycomb, the honeycomb preferably providing at least part of the support for the attenuating medium.

Additional objects and advantages of the invention are to provide total reliability and effectiveness by using no moving or electrical components, and by not depending upon materials which must be without flaws, imperfections, or other defects. Operation of the invention is possible using materials in common use for years, and is not dependent upon development of materials, means of manufacture, or analytical methods not currently available. Most significantly, the invention provides substantial attenuation of all types of pressure waves on the source side as well as the remote side of the pressure wave attenuating structure. In the case of proximate explosions, substantial reduction of both overpressure and thermal effects have been experimentally verified on the blast side as well as the opposite side of the pressure wave attenuating structure.

Further objects and advantages of the invention will become apparent form a consideration of the drawings and ensuing description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a panel configuration for the attenuating assembly of the invention. The panel assembly is preferably contemplated for containing an aqueous foam as the flowable attenuating medium. Accordingly, the assembly of FIG. 1 illustrates means for recycling and regenerating the aqueous foam within the confinement means.

FIG. 2 is a view taken along section lines II—II of FIG. 1 and better illustrates the interaction of the confinement means with the flowable attenuating medium.

FIG. 3 is a view similar to FIG. 2 and illustrates yet another embodiment of an acoustic/shock wave attenuating assembly according to the present invention which is placed between a structure to be protected from shock waves and other pressure wave phenomena transmitting in a surrounding liquid medium.

FIG. 4 illustrates a variation of the panel configuration wherein the side portions of the confinement means are articulated or corrugated in order to provide increased surface area and generate greater turbulence in the flowable attenuating medium, thereby producing even more effective attenuation for the acoustic/shock wave.

FIG. 5 is a view similar to FIG. 2 while illustrating multiple panel assemblies of similar construction with intervening gaps in order to even more effectively attenuate the acoustic/shock wave.

FIG. 6 illustrates yet another embodiment of an acoustic/shock wave attenuating assembly according to the present invention wherein the confinement means and the flowable attenuating medium contained therein are supported in common from a suitable structure.

FIG. 7 is a fragmentary view in section of a flowable attenuating medium for the assembly of the present invention formed from solid particulates.

FIG. 8 illustrates the arrangement of a plurality of panel assemblies each generally similar to that of FIG. 1 to form a generally enclosed prismatic chamber.

FIG. 9 illustrates yet another embodiment of an acoustic/shock wave attenuating assembly constructed according to the present invention wherein the panel combination of the confinement means and flowable attenuating medium forms a generally enclosed chamber. More specifically, the panel combination illustrated in FIG. 9 forms a cylindrical portion open at both ends.

FIG. 10 similarly illustrates such a panel combination formed generally as a dome to completely enclose a chamber therebeneath, with a section removed to show its construction.

FIG. 11 also similarly illustrates yet another configuration wherein the panel combination is arranged with an irregular shape to also form a chamber therebeneath open at one end.

FIG. 12 is a view of another embodiment of the acoustic/shock wave attenuating assembly of the present invention wherein the attenuating medium is formed as a flexible panel including solid particulates confined and also preferably supported by filamentary material.

FIG. 13 is an enlarged fragmentary view of a portion of a flexible panel similar to that of FIG. 8 but wherein the solid particulates are integrally formed with the filamentary material.

FIG. 14 illustrates a flexible panel formed from an attenuating medium comprised of solid particulates and filamentary material in generally a similar manner as in FIGS. 12 and 13, the flexible panel being usable as insulation, a cushioning component, curtain barrier or lining material for example.

FIG. 15 is a cross-sectional view of flexible panel as illustrated in FIG. 14 employed as a lining in a container.

FIG. 16 is a cross-sectional representation of an embodiment of the invention including a frangible element on an exposed surface of the attenuating medium.

FIG. 17 is a cross-sectional representation of still another embodiment of the invention illustrating its use in combination with armor plate or the like particularly for enhancing the ability of the armor plate to resist explosive devices such as shaped-charge devices.

FIG. 18 is a perspective representation of another embodiment wherein the attenuating medium is arranged in the cells of a honeycomb structure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The various drawing figures accordingly illustrate a number of embodiments according to the present invention. Those embodiments are summarized below followed by a more detailed description of the respective figures.

FIG. 1 is a perspective view of a basic version of the pressure wave attenuation device. The device comprises two mesh or perforated solid screens which are parallel or substantially parallel for planar configurations and concentric or substantially concentric for cylindrical, spherical or other three dimensional forms which can be generated by revolving a planar curve about an axis, with a pressure wave-attenuating fluid, such as aqueous foam or vermiculite beads, emplaced and filling the space between the mesh or perforated sheet screens. The screen elements may be flat or corrugated, or a combination thereof. The screen elements are either held in place by a rigid structural frame or by otherwise suspending and securing the lower edges of the screens to prevent their displacement. The minimum spacing between screens is preferably the least distance between perforations in perforated sheet screens or least dimension of mesh openings in mesh screens.

Additional embodiments of the invention are shown in FIGS. 2-15. As illustrated, the basic configuration can be modified with the addition of any combination of mesh screen, perforated solid, or solid materials connecting to the mesh or perforated sheet screens of the basic version of our invention, or to the frame members which comprise the edge supporting members of the screen elements of the FIG. 1 basic version, which would then form top, bottom, and side surfaces as shown in FIG. 2.

The invention may include one or more linings, as shown in FIG. 2. These linings may be connected or affixed to any of the mesh or perforated sheet screen elements, or to the structural members holding the screens in place, or may be suspended. Said linings may be in the form of a sealed enclosure or bag emplaced between the screen elements of the basic version of the invention, into which the pressure wave attenuating medium may be introduced.

Additional mesh or perforated sheet materials in any number or combination thereof between the screens comprise outer surfaces of the basic version of the invention to form interior screen elements in a sandwich configuration, thus forming a sandwich arrangement of a plurality of acoustic/shock wave attenuating assemblies as shown in FIG. 5. Linings may be emplaced between one or more of these interior screens and elements forming the outer surfaces of the invention. The preferred embodiment of the invention uses corrugated mesh screens to form the outer surfaces, flat mesh comprising the interior screen elements, waterproofed paper lining inside the screen elements and with aqueous foam filling the sandwich formed by the above elements.

The pressure wave attenuating fluid may be emplaced in the volume formed between an interior screen element and an outer screen, or between any two interior screen elements where a plurality of interior screen elements is employed, or in any combination of such spaces. This fluid may be aqueous foam, a gas emulsion, (wherein a gas is entrained and dispersed through a liquid matrix in the form of bubbles, with the gas bubble

diameters generally commensurate with the thickness of the liquid bubble walls), a gel (preferably with entrained gas), or granular or other solid particulates having necessary flow characteristics. Gas may be emplaced and confined by an enclosing element in one or more of the gaps between each sandwich assembly, with the gas pressure being equal to, greater than, or less than atmospheric or ambient pressure. Vacuum conditions may be generated in one or more of the gaps between each sandwich assembly.

The embodiments of the various figures are described in greater detail below.

Referring initially to FIG. 1, an acoustic/shock wave attenuating assembly is generally indicated at 10. Confinement means for the assembly comprises a screen or grid 12 arranged on four sides of the assembly to provide an enclosure for the flowable attenuating medium 14.

As illustrated in FIG. 1, the bottom of the assembly 10 is formed by a tray 16 while the top of the assembly is formed or enclosed by a plate 18. The tray 16 and plate 18 function in combination with the screen 12 to completely enclose the flowable attenuating medium 14 within the assembly 10.

The flowable attenuating medium 14 in the assembly of FIG. 1 is preferably contemplated as an aqueous foam of the type noted above. Since such aqueous foams are subject to deterioration wherein the foam degenerates into a gaseous phase and a liquid phase, the assembly 10 is adapted for recycling and regenerating the aqueous foam in order to assure that it fills the space within the assembly 10. The tray 16 serves to receive and collect the liquid phase from such deteriorated foam. The liquid is recycled through a line 20 by a pump 22 to a manifold 24 having multiple connections 26 through the upper plate 18 for returning regenerated foam to the assembly 10. Preferably, a source of gas 28 is provided for regenerating the foam within the manifold 24 so that it can flow downwardly into the assembly 10.

When aqueous foams are used as the flowable attenuating medium 14, they may be generated from any foamable agents, preferably those which are normally used in fire suppression. Such agents include hydrolyzed protein liquids, proteinaceous liquids with fluoropolymeric additives, along with a large number of synthetic surfactant and stabilizing chemical combinations. The foaming gas for use in the gas source 28 may be of a similarly wide range so long as the gas is not chemically reactive in a destructive manner to the stabilizing components in the bubble wall liquids. Foaming gases would preferably include inert elements such as argon or fire extinguishing compounds such as carbon dioxide, sulfur hexafluoride, or halogenated carbon agents (halons). Compressed air is also an acceptable foaming gas.

Referring now to FIG. 2, the screen 12 forming the confinement means for the flowable attenuating medium may not be sufficient for maintaining an aqueous foam within the assembly 10. Accordingly, FIG. 2 illustrates a preferred embodiment wherein a liner 30 is arranged inside the screen 12. The screen 12 formed from metal, plastic or the like thus remain very porous to the acoustic/shock wave. At the same time, the liner 30 serves to maintain the aqueous foam within the interior 32 of the assembly 10. At the same time, the liner 30 is also porous to the acoustic/shock wave as defined above. Preferably, the liner 30 is formed from paper or

film which is resistant to wetting by the aqueous foam. At the same time, the liner 30 tends to be readily ruptured by the shock wave so that it does not interfere with penetration of the shock wave into the attenuating medium 14 and thereby reduces the reflected overpressure that inevitably develops when shock waves impinge upon a solid surface. The liner 30 thus serves to even further attenuate the acoustic/shock wave in combination with the screen 12 and the flowable attenuating medium 14.

Referring now to FIG. 3, another embodiment of an acoustic/shock wave attenuating assembly is generally indicated at 10', and is placed in such an arrangement whereby the structure 34 is situated on the side of the assembly 10' opposite the liquid surrounding medium 36. A solid, non-porous membrane or rigid shell 37 provides confinement and isolation from the surrounding liquid medium 36 for an acoustic/shock wave transmitting liquid 38.

FIG. 4 illustrates yet another embodiment of the invention 10' which is substantially similar to that illustrated in FIGS. 1 and 2. However, the screen 12' in FIG. 4 is corrugated or articulated or otherwise configured to have a substantially increased surface area in order to more effectively attenuate the acoustic/shock wave. Additionally, the corrugations or articulations serve to greatly increase turbulence and formation of miniature shock waves, and thereby specifically and even more effectively attenuating shock waves.

Referring now to FIG. 5, another embodiment of an acoustic/shock wave attenuating assembly is generally indicated at 10' and comprises panels 10A, 10B and 10C similar to the overall panel assembly of FIGS. 1 and 2. The panels 10A, 10B, and 10C as illustrated in FIG. 3 are spaced apart to form intervening gaps indicated at 40. Thus, an acoustic/shock wave approaching the assembly of 10' of FIG. 5 laterally would be caused to sequentially penetrate the panels 10A, 10B and 10C as well as the intervening gaps in order to even more effectively attenuate the acoustic/shock wave. Otherwise, the various components for the multiple panels in the embodiment of FIG. 5 are indicated by similar primed numerals in FIGS. 1 and 2.

Referring now to FIG. 6, yet another embodiment of an acoustic/shock wave attenuating assembly is generally indicated at 50 and also includes components generally similar to those described in FIGS. 1 and 2. Accordingly, corresponding components in FIG. 6 are indicated by similar primed numerals. Generally, the screen or confinement means 12' in FIG. 6 is in the configuration of one or more bags for containing the flowable attenuating medium 14'. At the same time, the bags or confinement means 12' is suspended from a fabricated structure 52. The fabricated structure 52 thus tends to provide a panel configuration for the assembly even with the confinement means or bags 12' being very flexible by themselves.

Referring now to FIG. 7, another embodiment or variation of the flowable attenuating medium 14' is illustrated. The flowable attenuating medium 14' of FIG. 7 is formed from solid particulates 62 preferably having both mechanical properties and flow properties of a fluid. Also preferably, the solid particulates include means for resisting relative displacement of the particulates in order to better simulate characteristics of an aqueous foam. For such a purpose, the particulates 62 may be provided with a coating 64 to resist relative motion between the particulates while permitting flow

in accordance with the present invention. For example, the coating 64 may be a light adhesive or may even comprise Velcro type hook and loop fasteners for resisting relative movement between the particulates. It is noted that VELCRO is a trademark for such a hook and loop type fastener.

Solid particulates 62 may be of any shape, including spherical and irregular forms. The largest diameters or largest cross sectional dimensions of particulates used in this invention should be generally less than half the distance between the generally parallel screens 12. The solid particulates 62 should generally be macroscopic. These particulates may be hollow with solid surfaces, solid shells with internal cavities containing liquid phases, or may be comprised entirely of solid materials. The solid material may be a solid foam, such as a polyurethane or elastomeric compound, or otherwise be a sponge, whereby the gas and solid phases are both continuous, which thus distinguishes sponges from foams, wherein the gas phase is entirely enclosed within a liquid or solid continuous phase. Alternatively, the solid particulates may be comprised of entrapped gas phases, for example, in the nature of volcanic foam glasses, perlite, pumice or the like.

Any of the solid particulates of the invention may be flexible or elastic, or conversely may be rigid in their mechanical properties.

Referring now to FIG. 8, multiple panels 10D, 10E, 10F and 10G are formed in generally the same manner as the assembly 10 of FIG. 1. However, the panel assemblies 10D-10G are suspended or otherwise supported to enclose and define a chamber 90 which may also be used for a number of applications as described below.

With any of the embodiments of FIGS. 1-8, either the confinement means comprising the screen 12 and liner 30 and/or the flowable attenuating medium 14 itself may be formed from materials absorbing substantial additional energy from the acoustic/shock wave. For example, intumescent and ablative materials may be employed either as coatings, treatments for the lining 30, or as comprising materials of solid particulates 62 or coatings for these particulates 64. Alternatively, other materials which absorb thermal energy through an endothermic chemical reaction may be used as linings 30 or as treatments for these linings, or otherwise or in addition to coatings of the screen 12 and solid particulates 62 where these are employed.

FIGS. 9, 10 and 11 illustrate similar panel configurations, preferably multiple panels with intervening gaps, formed as generally rigid structures with enclosed shapes to substantially form a chamber therebeneath. These structures of FIGS. 9-11 may be employed in a number of applications as described in greater detail below.

Referring initially to FIG. 9, multiple panels 10A', 10B', and 10C' are commonly formed as a portion of a cylinder to define the chamber 70 therebeneath. The chamber is at the ends as illustrated.

FIG. 10 illustrates yet another arrangement of multiple panels, 10A', 10B' and 10C' configured as a dome forming a chamber 80 which is completely enclosed therebeneath. FIG. 10 provides a fragmentary section of the multiple panel assemblies 10A', 10B' and 10C' comprising the dome chamber 80.

FIG. 11 illustrates a relatively irregular configuration for similar panels 10A', 10B' and 10C' to form a chamber 90 which is substantially enclosed therebeneath

while being open at one end. Here again, such a configuration may be used to advantage in particular applications.

FIGS. 12-14 illustrate another embodiment of the invention wherein the attenuating medium 114 is formed by solid particulates 116 dispersed in a matrix of filamentary fibers 118. The solid particulates 116 and the filamentary fibers 118 together comprise a substantial portion of the solid phase for the attenuating medium 114. In this embodiment, the filaments serve to entrap the particulates while allowing them to experience limited displacement and oscillations induced by pressure waves passing through the medium. The allowed displacement of the solid particulates thus provides the ability for transmitting shock waves to generate turbulent flow fields among the solid particulates as well as for the filaments themselves to oscillate and further enhance turbulent flow field magnitude. Aerogel materials may be used to partially or entirely replace the attenuating medium 114, as described in greater detail below.

Within the embodiment of FIG. 12 and also in FIGS. 13 and 14, the filamentary material or fiber 118 also serves as a means for confining and preferably for supporting the solid particulates.

In this regard, FIG. 13 illustrates a flexible panel 120 formed from an attenuating medium 114 substantially similar to that of FIG. 12.

FIG. 13 illustrates a fragmentary section of attenuating medium 114' including solid particulates 116' and filamentary material or fibers 118'. In the embodiment of FIG. 13, the solid particulates 116' are formed as an integral portion of the filaments or fibers 118' in a manufacturing process described in greater detail below.

In the embodiment of FIG. 13 or in the embodiments of FIGS. 12 and 14, for example, the solid particulates and the filaments themselves may be solid or hollow. For example, cavities may be created in the solid particulates and/or in the filaments by the manufacturing process. The cavities (not shown) may be filled by a liquid, gas or powdered solid. In the case of powdered solids, they would preferably have a mean diameter of less than about 0.1 millimeters.

Referring also to FIG. 15, the flexible panel 120 may be employed as a liner 120' in a container 122. In this manner, the liner 120' may be employed for containing pressure conditions including acoustic and/or shock waves as disclosed above, generated for example by means of an explosive device 124.

Referring in combination to FIGS. 14 and 15, the flexible panel 120, optionally employed as a liner 120' in FIG. 15, consists of solid particulates and filamentary fibers as disclosed above. The flexible panel may be used in order to mitigate deleterious effects produced by an explosion resulting from the device 124 in the container 122. Such a configuration might be employed for example where the container 122 is a cargo carrying hold with the explosive device 124 being a part of the cargo.

In such a configuration, the attenuating medium 120 can be made by introducing substantial quantities of the solid particulates into a batch process as is typically used in the manufacture of glass fiber insulating batts (not otherwise shown). Uncured binder (also not shown) may be used to weakly attach solid particulates to the glass filaments to the desired extent in this embodiment of the attenuating medium.

The attenuating medium of FIGS. 12 and 13 may be used as a filler in assemblies such as illustrated in FIG. 1, for example, or may act as an attenuating assembly in and of itself wherein the attenuating assembly is used as a lining or otherwise suspended.

The attenuating medium of FIGS. 12 and 13, for example, may be formed for example from conventional insulating materials, preferably a variety of minerals well known to those skilled in the art. For example, thermal insulation of a type suitable for forming the attenuating medium 114 may be a material available for example from Schueller International Corporation under the trademark MIN-K and in a variety of configurations. Such a material includes both the solid particulates 116 and filamentary fibers or material 118 as illustrated in FIG. 12. Furthermore, such materials may be provided with a variety of other characteristics adding superior performance in the attenuating medium of the invention. Such characteristics include low conductivity, reduced conductivity at high altitudes, low thermal diffusivity, flexibility, the capability of being molded, etc. These materials are also available in forms lending themselves to bonded together or to other materials and may be obtained with special coatings such as silicones and the like.

As noted above, the attenuating medium 114 of FIG. 12 may include a variety of materials forming both the solid particulates and the filamentary material. For example, the filamentary material may be fiberglass or a variety of other minerals or plastics for example. The solid particulates may be formed from the same material as the filamentary material or from other materials such as vermiculite, perlite, pumice, hollow glass beads, etc.

The solid particulates and/or the filamentary material may be more densely distributed in selected regions of the attenuating panel in order to achieve focusing and/or diffraction of pressure conditions passing there-through. The solid particulates and filamentary material may also preferably be formed from materials of high reflectivity in the infrared portion of the electromagnetic spectrum or such materials may be formed on surfaces of the solid particulates and/or filamentary material. Such a high reflectivity material may include titanium, for example in titanium dioxide. As noted elsewhere, materials in the solid particulates and/or filamentary material may also be selected with characteristics for extinguishing combustion reactions.

The invention may operate as a partition, lining, container, barrier or barricade, wall element, or structure standing independent of any exterior need of support or attachment. The invention may operate as an acoustic or shock wave barrier, simultaneously be employed for attenuation of all types of pressure waves, or for protection exterior to the invention or on either side of the invention when employed as a partition or wall structure. The invention may also operate as an acoustic wave absorber for protection of spaces either formed by the invention or in which partitions or lining elements of which variants of the invention comprise a part are situated. The invention may serve a secondary purpose as reservoir of fire fighting aqueous foam agents.

The basic version of the invention becomes operable when the pressure wave attenuating fluid is emplaced between two adjacent screen elements. Pressure waves impinging on the invention from any angle are reflected when they encounter screen and solid elements of the invention, and are admitted into the flowable attenuating medium when the incident waves encounter the

porous openings. Pressure waves transmitting through the outer screen element are substantially slowed and scattered as they travel through the flowable attenuating medium, particularly where this medium is an aqueous foam.

Portions of the transmitting waves are reflected upon encountering the second, or rear, screen of the acoustic/shock wave attenuating assembly and the gas (or vacuum, as may be employed)/fluid interface, and remaining portions of transmitting pressure waves are dispersed as they encounter the interface between the pressure wave attenuating fluid and contiguous gas or solid. A substantial fraction of the initially incident pressure wave will thus undergo multiple reflections within the fluid confined between screen elements, in essence, substantial portions of the incident pressure wave are trapped within the screen/fluid sandwich. With a plurality of screen/fluid sandwich layers, this effect will be magnified.

When aqueous foams are used, substantial energy is removed from the incident pressure wave by scattering at the multitudinous interfaces presented by bubble wall liquids and the gas entrapped which comprise: the basic units of aqueous foam structures, and through the displacement of the liquid in the aqueous foam. A similar effect is obtained when solid bead materials are employed—particularly solids with entrained gas, such as vermiculite and organic solid foams. For the particular case of aqueous foams, substantial energy is also removed from pressure waves reflected back into the attenuating fluid from screen components due to turbulent flow fields established by passage of the initial pressure wave. This is impossible for solid foam materials.

Additional energy and thus attenuation of transmitting pressure waves is accomplished by cancellation as scattered, slowed and reflected waves become coincident. A further contributor toward energy removal by the invention is that propagation paths of pressure waves through the foam are substantially lengthened by their scattering and dispersion.

Incident shock waves are attenuated by additional phenomena generated by the invention. Shock and blast waves consist of an initial overpressure, or positive pressure phase (in excess of the ambient initial pressure) followed by a negative, or rarefaction, phase. The rarefaction phase is typically longer in duration unless the shock wave undergoes reflections. Because shock waves transmitting through aqueous foams are substantially slowed and thereby further expanding the rarefaction wave duration relative to the overpressure portion, and at different values due to random dispersion within the foam, destructive interference by coincidence of positive and negative pressure waves is substantially increased with respect to unconfined aqueous foams or foams in simple containers.

Another substantial factor related to destructive interference between pressure wave components is that weaker (slower) shock waves have been shown to separate into two components when transmitting through aqueous foams. The precursor wave is lower in amplitude but propagates at a higher velocity. The main wave follows, it is larger in magnitude but tends to lose velocity with respect to the precursor wave during passage through aqueous foam. The present invention uniquely utilizes this phenomenon in two ways, by slowing strong shock wave propagation until the wave separates into precursor and main wave components, then causing reflecting of the two components in such a

manner as to promote destructive interference or cancellation.

Additionally, shock waves displace bubbles and accelerate liquids in bubble walls of the aqueous foam, causing the bubbles to shrink and many to collapse. This displacement of the liquid, the breaking of bubble walls against the cohesive force of their surface tension, and the acceleration of liquid droplets formed from shattered bubble walls all serve to absorb substantial energy from the transmitting shock wave. Substantial parts of the transmitting shock wave are reflected back into the aqueous foam at the interface between the foam and contiguous gas or solid, a process which is repeated numerous times by part of the original incident pressure wave, in essence trapping part of the original incident pressure wave.

Yet another substantial contributor to energy removal from the incident shock wave, thus attenuating such waves, is that the incident wave creates choked flow conditions within the mesh or perforated sheet openings, which serves to reflect a portion of the incident shock wave. In this manner, only a fraction of the energy carried by the incident shock wave is allowed to pass through the first screen encountered. Where the transmitted shock encounters another screen, another fraction of this shock wave is reflected back. When the reflected wave must travel through aqueous foam dispersion and attenuation of the wave is greatly increased through the phenomena described in the preceding paragraph. Turbulent flow fields are also established in the vicinity of screen elements by shock wave passage through screen openings, which significantly contribute to scattering of pressure waves within the foam and by transmitting pressure waves beyond.

Employment of an intervening evacuated space, a space filled by gas, or a space filled with solid particulates in which a vacuum or gas is present between spaces filled with aqueous foam or other flowable attenuating media will greatly increase pressure wave attenuation. Evacuated or vacuum spaces will not transmit pressure waves. Incident pressure waves will reflect at the solid surface which confines the vacuum or gas unless sufficiently intense as to rupture the confining surface. Upon rupture of the confining surface, the pressure wave would be transmitted by the flowable attenuating medium accelerated through the rupture, and the ambient gas able to leak into the formerly evacuated space. However, only a small portion of the incident pressure wave could be conveyed in this manner due to the small mass and irregular structure of accelerated, unconfined flowable attenuating medium. Further reflection and scattering of the transmitted pressure wave occurs upon encountering successive screens, linings, and foam interfaces.

Employment of corrugated screens in any location of the invention provides additional scattering and turbulence, which therefore further increases attenuation. Pressure waves impinging on the flowable attenuating medium from a gaseous medium arrive at the corrugated interface at differing times and at different angles. Scattering and dispersion of the transmitting pressure waves is thus enhanced. Furthermore, the path through the flowable attenuating medium is thus greater for a fraction of the transmitting pressure wave from the instant of first encounter with the foam. Since aqueous foam is known to substantially reduce the propagation velocity of pressure waves, further dispersion and de-

structive interference of transmitting wave components is accomplished when they are.

Linings serve to provide confinement for aqueous foams, and for solid particulate materials when these are employed. Some reflection of incident pressure waves will occur upon impingement, and such linings may provide additional acoustic barrier capabilities. Where the invention is employed primarily for blast and shock wave attenuation, linings and any other materials used to confine gases or maintain vacuum conditions must rupture or otherwise provide openings upon the impingement of shock waves at a pressure substantially below that of the impinging shock wave in order to avoid substantial pressure rise as is inevitably created by solid obstructions in these situations.

Coatings or chemical additions which serve to absorb thermal and radiant energy may be used on any element or combination of elements comprising the invention. Such chemicals reduce the energy of incident blast waves due to the mathematical linkage between blast wave temperature, overpressure, and propagation velocity, which serves to enhance attenuation of the incident blast wave. The invention operates with or without the presence of an increase in temperature, however, so that thermal energy absorbing materials only serve to enhance capabilities in certain applications.

Accordingly, the pressure wave attenuating device can be used for any type of pressure wave transmitted in a gaseous medium. The invention requires no electric power source or sensor to operate since aqueous foam generation and filling can be accomplished using only a compressed gas source with which to create and mechanically place the foam within the desired space or spaces. There are no electronic or mechanically sensing components which can prevent the invention from functioning. An additional advantage of the pressure wave attenuating device is that other energy absorbing or protective features may be added to enhance its attenuating capabilities or to provide additional capabilities, such as stopping fragments from explosions. Typical applications would enable the same aqueous foam agents and generating equipment as are commonly used in fighting fires to be employed in the invention.

Attenuation of acoustic waves is accomplished without regard to intensity, directionality, or frequency. This device operates regardless of orientation with respect to impinging pressure waves or, where present, confining walls defining an enclosure in which the invention is placed. Because of the light weight of aqueous foams and the structural elements required by the attenuating assembly described above, this invention is easily made portable in sizes useful for noise suppression around aircraft with jet or gas turbine engines. When protected from heat and sunlight, aqueous foams are stable for prolonged periods enabling the pressure wave attenuating device to be employed as acoustic walls in anechoic chambers or other applications requiring acoustic wave damping in enclosures.

Simultaneous attenuation of all types of pressure waves affords the invention the capability to serve as means to dispose of explosives and ordnance near structures or inhabited areas. By mitigating blast energy, noise and shock waves are attenuated. Bomb fragments are stopped by a combination of reducing propelling energy and by multiple layers of high strength screen materials. These same capabilities enable this device to be employed to provide protection of artillery crews exposed to enemy artillery and air dropped munitions

from both blast effect and from the noise produced by their own guns.

The ability of the pressure wave attenuating device to operate in a variety of configurations enables it to be employed to provide blast protection on board aircraft which may carry explosive devices meant to destroy the aircraft, and for protecting personnel sent to remove or disarm such devices when discovered. The invention can be configured to operate in curved spaces such as missile launchers used aboard warships, around machinery in hazardous environments such as in petrochemical refining and production facilities, or as protective barriers around rescue equipment. Our pressure wave attenuating device is unique in its ability to operate effectively in unconfined environments. Furthermore, our invention operates effectively without a requirement to be located close to the source of the pressure wave, or without a specific orientation thereto.

Furthermore, the variety of configurations allowed by this invention enable the acoustic/shock attenuating assembly to be employed for protecting ships and offshore structures from shock effects arising from underwater explosions when aqueous foams are employed as the flowable attenuating medium. The invention can similarly be used for protecting offshore and coastal structures from seismic shock effects as well as aquatic life from any type of shock waves in water. This can be accomplished by using a lining which confines a fluid which serves to transmit the pressure wave between the outer screen and a lining which confines aqueous foam in the manner of sonar type acoustical detection devices wherein a membrane is filled with water or other fluid to conduct acoustic waves.

The invention preferably employs aqueous foam agents which have neither toxic qualities nor produce toxic compounds as a result of operation. It is light in weight and may easily be stowed in most of its configurations when not needed or when being transported. When used in confined spaces, the invention occupies a small fraction of the enclosed volume and does not involve flooding. The acoustic/shock wave attenuating assembly enables personnel to occupy and work in that space, which only explosion vents allow among all possible blast pressure mitigating means in current use. Unlike explosion vents however, the invention uniquely is usable in situations which proscribe opening confined spaces to adjoining spaces. This is critical aboard ships, which cannot be opened to the sea, and within any structure where smoke and combustion products must be confined to avoid harm to trapped individuals and to facilitate emergency crew operation.

In addition to the use of solid and liquid attenuating mediums as described elsewhere, the invention further contemplates that substantially all embodiments of the invention are adapted for use with a class of very light weight materials generally referred to as "aerogels". These materials are similar in structure, at least in certain aspects, to the filamentary materials described in one of the preceding embodiments of the invention. However, the aerogels differ in their formation by the inclusion of multitudinous small cavities filled with a gaseous phase. Such aerogels can be manufactured with extremely low densities, almost down to that of atmospheric air at sea level, and have long been known to those skilled in the art of low density structures, etc.

Rather than describing such aerogels in greater detail herein, it is noted that the structure and typical compositions of such aerogels are described in a number of

references, particularly an article by Jochen Fricke, entitled "Aerogels", *Scientific American*, Vol. 258, No. 5, May 1988, pp. 92-97. This reference is incorporated herein as though set forth in its entirety.

It is to be understood that such aerogels, because of their extremely low density, are desirable for forming variations of substantially any of the embodiments of the invention where minimum weight is important. It is further noted that a flowable attenuating medium formed from aerogels may use generally the same support structures disclosed for the attenuating medium in different embodiments of the invention. Accordingly, the attenuating medium described in substantially all of the embodiments of the present invention may be replaced partially or entirely by such aerogel materials.

A further embodiment of the invention is described immediately below with reference to FIG. 16 which illustrates the use of an attenuating medium in combination with a frangible element or covering.

Referring to FIG. 16, an attenuating assembly generally similar to that indicated at 10 and 10' elsewhere, is indicated at 130. The assembly 130 includes a confinement means or support medium 12' in combination with a flowable attenuating medium 14'. The attenuating medium may be any of the forms described elsewhere herein.

A frangible element 132 is provided as a protective covering for the assembly 130 and particularly for the attenuating medium 14'. The frangible element 132 is arranged on the blast side or exposed side 136 of the assembly and opposite the protected side 138 of the assembly.

A stiffener 134 is preferably associated with the frangible element 132 if necessary or desired for further support.

This embodiment with the frangible element enables the attenuating assembly to withstand severe outdoor weather environments and to otherwise isolate the environment on one side of the attenuating assembly from the other.

The frangible element 132 is preferably formed as a part of the assembly 130 in order to prevent gas movement or diffusion through or across the assembly 130.

Frangible materials suitable for forming the element 132 are well known to those skilled in the art and may be formed, for example, from scored metal, composites of plastics and glass, plastics, glasses and other polymeric materials. Alternatively, they may also be formed from agglomerations of organic and/or inorganic materials held together by binders and pressed or molded into any desired shape.

The frangible element 132 is preferably designed to withstand wind loads or other common environmental conditions. At the same time, the frangible element 132 is adapted for shattering into small pieces when impinged upon by acoustic level pressure conditions including acoustic waves and/or shock waves as discussed elsewhere herein. Accordingly, when such pressure conditions arise, the shattering of the frangible element 132 immediately exposes the attenuating medium 14' to accomplish its function as described herein.

Still another embodiment of the invention contemplates its use for protecting structures and/or people from the harmful effects of explosive devices including ammunitions, bombs and other types of explosive devices. A particular type of ammunition against which the present invention can provide protection is generally referred to as either a shaped-charge or hollow-

charge device. By a combination of substantially reducing the velocity of the shock wave created by the detonation of the shaped-charge development of the blast front which forms a penetrating metal slug and entrainment by the attenuating medium, the penetrating ability of the slug formed by the shaped-charge munition or device is greatly reduced.

Such shaped-charge devices and their use are well known to those skilled in the art and a detailed description of such devices is not believed necessary within the scope of the present invention. It is noted that such shaped-charges and their functions are described by a large number of references, such as the publication *Fundamentals of Shaped-Charges* by William P. Walters, published 1989 by John Wiley & Sons, Inc. (see pp. 13-14, et al.). This reference is also incorporated herein as though set forth in its entirety.

The use of the present invention in such applications is illustrated in FIG. 17. Referring to FIG. 17, an attenuating assembly is generally indicated at 140 including a confinement means or support medium 12' in combination with a flowable attenuating medium 14' as described elsewhere herein.

In the embodiment of FIG. 17, the attenuating assembly 140 is arranged upon an otherwise exposed surface 142 of typical armor plate generally indicated at 144.

The attenuating assembly 140 preferably and optionally includes an actuating element or support surface 146 arranged either within or opposite the attenuating medium 14' from the exposed surface 142 of the armor plate.

When used to protect against the penetration and subsequent harmful effects from shaped-charge munitions, the assembly 140 can be used as an exterior armor or barrier element for a wide variety of implements or structures (not shown) including armor plate such as that indicated at 144 in FIG. 17. The incorporation of combustion-extinguishing agents, particularly those with rapid reaction times, greatly interferes with the formation of an effective penetrating slug, as shaped-charge munitions are intended to produce, and further reduces the damage possible behind the armor or barrier should it be pierced, particularly due to hot spall and blast gasses under pressure.

These mitigating events are produced by reducing the velocity of the shock wave which forms the penetrating slug, dispersing and scattering elements of the shock wave so as to disrupt the uniform shape of the shock wave front, to suppress to a substantial degree the evolution of blast gasses which constitute the motive force of the slug, and the subsequently formed jet to entrain materials of low mass into the slug and thus accelerate the disruption of the jet's mechanical integrity, and to suppress to a substantial degree the thermal energy component which comprises a substantial portion of the deleterious effects generated by the shaped-charge munition. Incorporation of a low-boiling point or flashing liquid within the attenuating assembly is possible with the present invention, which can further accelerate disruption of the slug as vapor bubbles are entrained.

Accordingly, it is particularly contemplated that this embodiment of the invention be employed in military or terrorist applications or the like.

Shaped-charges of the type referred to above generally fit the definition of the present invention in exceeding sonic or shock wave speeds.

Generally, the present invention can be useful against shaped-charges including only the attenuating medium 14' in combination with the armor plate as illustrated in FIG. 17. In such a combination, the shaped-charge may or may not be actuated upon contact with the medium 14' itself. In any event, the shaped-charge device is detonated upon contact with the exposed surface 142 of the armor plate 144. Assuming actuation upon contact with the armor plate, the shaped-charge device is generally surrounded by the attenuating medium 14' upon detonation so that the attenuating medium interferes with proper operation of the shaped charge as described above.

It is also possible to employ the attenuating medium 14' together with the actuating element or surface 146 which may form a portion of the confinement means or support medium 12'. In this regard, the actuating element 146 is selected with sufficient mass or resistance in order to assure actuation of the shaped-charge device. Thus, with the actuating element 146 in place, actuation of the shaped-charge device is assured as it approaches the attenuating medium 14' prior to engagement with the armor plate 144.

It is to be noted that shaped-charge devices of the type described above may include sequential charges. The embodiment of FIG. 17 with the actuating element 146 may be desirable in connection with such devices since an initial smaller charge would be actuated by the actuating element 146. Thereafter, the main charge of the device would be actuated upon engagement with the armor plate with the device being surrounded by the attenuating medium as described above. It is further contemplated that spaced apart layers of the attenuating medium, either alone or in combination with suitable support structure (not shown) may be employed for even further protection against shaped-charge devices including sequential charges.

Another embodiment or concept of the invention is similarly contemplated for protecting people and/or structures from the harmful effects of explosions where explosive ammunitions or devices, for example, may be detonated due to shock wave over-pressure and/or thermal energy release from the detonation of another explosive charge or device. This phenomenon is commonly referred to as "sympathetic detonation", "fratricide", "propagation" or "chain reaction". Any of the embodiments of the present invention may be employed in such applications as a barrier, buffer or ramp of one explosive munition or device in order to protect it from external overpressure and/or thermal energy generated by another explosive device arranged external of the invention.

Accordingly, in this embodiment or concept, the attenuating medium is used in generally the same manner described elsewhere herein. However, it is contemplated that one explosive element or device (not shown) be sheltered or arranged within the attenuating medium assembly of the invention in order to protect it from another explosive element or device (not shown) which is external to the attenuating medium assembly.

A still further embodiment or variation of the invention involves its use in forming air cargo containers or the like. Here again, generally all of the above described embodiments of the invention are suitable for this application with the air cargo container forming the interior of the attenuating medium assembly. Preferably, the assembly is formed as a complete enclosure or lining for the container. It is also particularly contemplated that

the invention be used in fabricated panels to form the lining for such containers.

In any event, a container including such a lining can provide substantial protection against blasts occurring within the container, the invention thereby protecting the areas surrounding the container. Similarly, the lining could also protect the interior of the container from external blasts.

Referring particularly to FIG. 18, the invention also contemplates use of the attenuating medium of any of the preceding embodiments in combination with conventional honeycomb which may preferably provide support for the attenuating medium. A preferred configuration is indicated at 150 in FIG. 8 wherein the attenuating medium 14' is preferably arranged in all of the cells 152 of a honeycomb structure 154. The attenuating medium is illustrated only in selected cells of the honeycomb structure in FIG. 18 for simplicity.

The attenuating medium may be a solid or liquid as described elsewhere above.

Preferably, the configuration 150 includes porous confinement means 30' arranged on opposite sides of the honeycomb structure 154. The cells 152 of the honeycomb structure are arranged with their axes 156 intersecting the porous confinement means 30'. The configuration 150 is preferably arranged with one of the porous confinement means 30' facing a shock wave source as indicated by the arrow 158.

With this arrangement, the cells of the honeycomb are exposed to the shock wave as it penetrates porous confinement means 30'. Thus, the attenuating medium is free to react in generally the same manner described above. Preferably, the cells of the honeycomb are sufficiently large to permit the contemplated function of the attenuating medium.

More preferably, the honeycomb structure 154 is provided with a large number of openings 160 in the walls 162 of the cells. The openings 160 permit lateral propagation of the shock wave between adjacent cells to further facilitate the function of the attenuating medium as discussed elsewhere herein.

There have accordingly been described a number of embodiments of attenuating assemblies and/or mediums constructed according to the present invention. Variations and modifications in addition to those described above are believed obvious from the description. Accordingly, the scope of the invention is defined only by the following appended claims which are also further exemplary of the invention.

What is claimed is:

1. An assembly for attenuating acoustic level pressure conditions, comprising

a flowable attenuating medium exhibiting aqueous foam characteristics, namely the ability of acting in the nature of a liquid mass to resist relative displacement by surface tension and viscous forces and the ability to substantially scatter and disperse pressure conditions transmitting therethrough by virtue of multitudinous curved surfaces dividing different phases, and enabling the generation of turbulent flow fields by transmitting pressure conditions, and

confinement means for containing and supporting the flowable attenuating medium, the combination of the confinement means and flowable attenuating medium being arranged for intercepting the pressure conditions to be attenuated, the confinement means being porous with respect to the pressure

- conditions for allowing the pressure conditions to penetrate the flowable attenuating medium, the porous confinement means also causing substantial pressure decrease of pressure conditions penetrating the porous confinement means, the confinement means comprising generally parallel side portions combining to form a panel with the flowable attenuating medium being supported therebetween for intercepting pressure conditions approaching one of the side portions.
2. The attenuating assembly of claim 1 wherein both side portions of the confinement means are porous with respect to the pressure conditions in order to achieve more effective attenuation thereof.
3. The attenuating assembly of claim 2 further comprising a plurality of panels each formed by generally parallel side portions with the flowable attenuating medium being supported therebetween, and intervening gaps between the panels whereby the pressure conditions are effectively caused to successively penetrate the plurality of panels and intervening gaps in order to achieve even more effective attenuation.
4. The attenuating assembly of claim 3 further comprising structural means for supporting the combination of the confinement means and the flowable attenuating medium.
5. The attenuating assembly of claim 4 wherein the combination of the confinement means and the flowable attenuating medium is shaped to form a generally enclosed chamber.
6. The attenuating assembly of claim 1 wherein the flowable attenuating medium is an aerogel.
7. The attenuating assembly of claim 1 arranged on an exposed surface of armor plate in order to enhance the ability of the armor plate to resist explosive devices.
8. The attenuating assembly of claim 7 wherein the assembly further comprises an element arranged in spaced apart relation from the armor plate for actuating shaped-charge devices approaching the attenuating assembly.
9. The attenuating assembly of claim 1 further comprising a frangible shield associated with the flowable attenuating medium for normally separating environmental conditions on opposite sides of the attenuating medium, the frangible shield being subject to shattering by the acoustic level pressure conditions in order to facilitate reaction of the flowable attenuating medium to the pressure conditions.
10. The attenuating assembly of claim 9 further comprising a stiffener element arranged in supporting relation with the frangible shield.
11. The attenuating assembly of claim 1 forming a lining for at least one surface portion of a container.
12. The attenuating assembly of claim 1 wherein the flowable attenuating medium is an aqueous foam.
13. The attenuating assembly of claim 12 further comprising means for regenerating aqueous foam from liquid draining from the aqueous foam in the confinement means and thereby maintaining the aqueous foam so that its volume substantially fills the confinement means.
14. An assembly for attenuating acoustic level pressure conditions, comprising
a flowable attenuating medium exhibiting aqueous foam characteristics, namely the ability of acting in the nature of a liquid mass to resist relative displacement by surface tension and viscous forces and the ability to substantially scatter and disperse

- pressure conditions transmitting therethrough by virtue of multitudinous curved surfaces dividing different phases, and enabling the generation of turbulent flow fields by transmitting pressure conditions, and
- confinement means for containing and supporting the flowable attenuating medium, the combination of the confinement means and flowable attenuating medium being arranged for intercepting the pressure conditions to be attenuated, the confinement means being porous with respect to the pressure conditions for allowing the pressure conditions to penetrate the flowable attenuating medium, the porous confinement means also causing substantial pressure decrease of pressure conditions penetrating the porous confinement means, the attenuating medium being arranged in a honeycomb structure.
15. The attenuating assembly of claim 14 wherein the honeycomb is formed with cells having axes arranged for flow of the acoustic level pressure conditions through the cells of the honeycomb.
16. The attenuating assembly of claim 15 wherein the cells are formed by walls having openings interconnecting adjacent cells of the honeycomb.
17. An attenuating panel for attenuating acoustic level pressure conditions, comprising
multitudinous solid particulates having a dimension of at least about 1 millimeter, and
filamentary material forming a matrix for the solid particulates,
the filamentary material having mechanical integrity for providing confinement of the solid particulates in the matrix of filamentary material while allowing the solid particulates to be relatively displaced by interaction with the pressure conditions whereby the panel is capable of scattering and dispersing pressure conditions passing therethrough and further enabling formation of turbulent flow fields within the attenuating panel from the pressure conditions.
18. The attenuating panel of claim 17 further comprising means interacting with the solid particulates and filamentary material to increase resistance of the solid particulates to relative displacement by the pressure conditions in addition to resistance attributable to inertia forces, the attenuating panel being porous throughout a dimension corresponding to passage of the pressure conditions therethrough.
19. The attenuating panel of claim 18 wherein the means interacting between the solid particulates and the filamentary material is an adhesive substance.
20. The attenuating panel of claim 17 wherein the solid particulates comprise an entrained gaseous phase.
21. The attenuating panel of claim 17 wherein the solid particulates are mechanically trapped by multiple strands of the filamentary material.
22. The attenuating panel of claim 17 wherein the solid particulates are more densely distributed in selected regions of the attenuating panel.
23. The attenuating panel of claim 17 wherein the multitudinous solid particulates are integrally formed with the filamentary materials.
24. The attenuating panel of claim 23 wherein the solid particulates each generally have a dimension of at least about 1 millimeter.
25. The attenuating panel of claim 17 further comprising one or more additional and similar attenuating pan-

27

els in generally parallel arrangement with each other and forming intervening spaces.

26. The attenuating panel of claim 17 arranged to form an enclosed chamber.

27. The attenuating panel of claim 17 forming a lining for at least one surface portion of a container.

28. The attenuating panel of claim 17 arranged on an exposed surface of armor plate in order to enhance the ability of the armor plate to resist explosive devices.

29. The attenuating assembly of claim 28 wherein the assembly further comprises an element arranged in spaced apart relation from the armor plate for actuating

28

shaped-charge devices approaching the attenuating assembly.

30. The attenuating panel of claim 17 further comprising a frangible shield associated with the flowable attenuating medium for normally separating environmental conditions on opposite sides of the attenuating medium, the frangible shield being subject to shattering by the acoustic level pressure conditions in order to facilitate reaction of the flowable attenuating medium to the pressure conditions.

31. The attenuating panel of claim 30 further comprising a stiffener element arranged in supporting relation with the frangible shield.

* * * * *

15

20

25

30

35

40

45

50

55

60

65



US005910540A

United States Patent [19]**Takahashi**[11] **Patent Number:** **5,910,540**[45] **Date of Patent:** **Jun. 8, 1999**[54] **THERMOPLASTIC ELASTOMER
COMPOSITION AND COMPOSITE MOLDED
PRODUCT**[75] **Inventor:** **Hideki Takahashi, Mie, Japan**[73] **Assignee:** **Mitsubishi Chemical Corporation,
Tokyo, Japan**[21] **Appl. No.:** **08/734,600**[22] **Filed:** **Oct. 22, 1996**[30] **Foreign Application Priority Data**

Nov. 6, 1995 [JP] Japan 7-287245

[51] **Int. Cl.⁶** **C08L 53/02; C08L 67/02;
C08L 75/04; C08L 77/00**[52] **U.S. Cl.** **525/92 B; 525/92 C; 525/92 F**[58] **Field of Search** **525/92 F, 92 B,
525/92 C**[56] **References Cited****U.S. PATENT DOCUMENTS**

4,994,508	2/1991	Shiraki	525/92 F
5,002,625	3/1991	Naritomi	156/245
5,149,589	9/1992	Naritomi	428/412
5,439,976	8/1995	Kinoshita	525/92 F

OTHER PUBLICATIONS

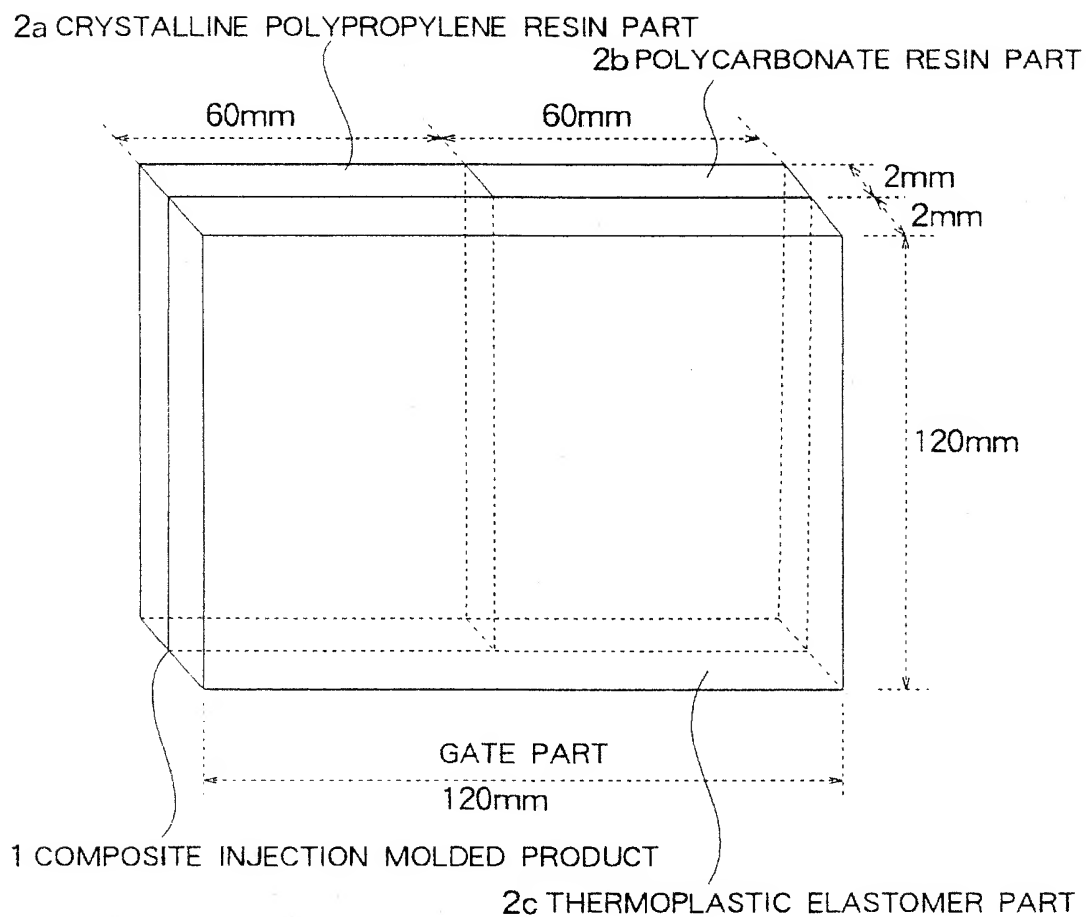
Hytrel 4056, Dupont product bulliteu HYT-102A.

Primary Examiner—Patricia A. Short*Attorney, Agent, or Firm*—Oblon, Spivak, McClelland,
Maier & Neustadt, P.C.[57] **ABSTRACT**

The present invention relates to a thermoplastic elastomer composition comprising the following components (A) and (B), and to a composite molded product comprising a resin layer and an elastomer layer containing said composition as the base material. Component (A): 5 to 95% by weight of a styrene type block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond unit. Component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of polyester type thermoplastic elastomers, polyamide type thermoplastic elastomers, and polyurethane type thermoplastic elastomers. The composition of the present invention exhibits excellent heat fusion properties to both an olefin type resin and a nonolefin type resin, and gives a composite molded product having a high peeling strength, comprising said resin and said elastomer.

11 Claims, 1 Drawing Sheet

FIG. 1



THERMOPLASTIC ELASTOMER COMPOSITION AND COMPOSITE MOLDED PRODUCT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a thermoplastic elastomer composition with excellent heat fusion properties which can be bonded not only to a layer of an olefin type resin represented by a propylene type resin, but also to a layer of a nonolefin type resin such as an aromatic polycarbonate, acrylic resin, styrene type resin, vinyl chloride type resin, and a modified polyphenylene ether resin, to a composite molded product produced therefrom, and to a process for producing said composite molded product.

2. Description of the Prior Art

Conventionally, when (1) a crystalline olefin type resin layer and a polyester type thermoplastic elastomer, polyamide type thermoplastic elastomer or polyurethane type thermoplastic elastomer are to be combined together to produce a laminate, or (2) a nonolefin type resin layer such as an aromatic polycarbonate, acrylic type resin, and styrene type resin and an olefin type thermoplastic elastomer or styrene type thermoplastic elastomer are to be combined together to produce a laminate, since they are a combination of materials which can not be fusion-bonded together, such methods have been employed to produce composite products therefrom. In such methods, a combination of a recess and a projection are provided at the joint of the two different materials, a core material is partially covered with a surface material, or a hole is provided in a core material so that a surface material reaches the back side, to thereby bond them together mechanically, or an adhesive such as a primer is applied on the joint to make them into a composite molded product.

Accordingly, the resulting composite molded product has such problems as poor bonding strength between both layers, overly complicated structure or too many production steps.

As an attempt to solve such a problem, a method has been proposed in which an elastomer having polarity such as a polyester type thermoplastic elastomer, polyamide type thermoplastic elastomer, or polyurethane type thermoplastic elastomer is added to a nonpolar elastomer such as an olefin type thermoplastic elastomer, styrene/ethylene/butylene/styrene copolymer (hereinafter also simply abbreviated as "SEBS"), or styrene/ethylene/propylene/styrene copolymer (hereinafter also simply abbreviated as "SEPS"), as described in U.S. Pat. Nos. 5,002,625 and 5,149,589, or Japanese Patent Laid-open Nos. 2-147306 and 6-65467.

However, according to the method in which a polyester type thermoplastic elastomer, polyamide type thermoplastic elastomer or polyurethane type thermoplastic elastomer is added to an olefin type thermoplastic elastomer, SEBS or SEPS, the polyester type thermoplastic elastomer, polyamide type thermoplastic elastomer or polyurethane type thermoplastic elastomer is added in an increased amount that the resulting heat fusion property to the nonolefin type resin layer becomes satisfactory, the heat fusion property to the crystalline olefin type resin layer becomes almost nothing on the contrary.

Thus it has been difficult to carry out heat fusion to both the crystalline olefin type resin layer and the nonolefin type resin layer, and 1) heat fusion to the nonolefin type resin layer requires the olefin type thermoplastic elastomer, SEBS

or SEPS to which the polyester type thermoplastic elastomer, polyamide type thermoplastic elastomer or polyurethane type thermoplastic elastomer is added, while 2) heat fusion to the crystalline olefin type resin layer requires a normal olefin type thermoplastic elastomer or styrene type thermoplastic elastomer; and this situation has led to such problems as a complicated molding process and a misuse of the molding material.

It has also been impossible to produce a composite molded product with a three layer structure comprising a nonolefin type resin layer/thermoplastic elastomer layer/crystalline olefin type resin layer.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide a thermoplastic elastomer composition containing a specific styrene type block copolymer which has good heat fusion properties in regards to both olefin type resins and nonolefin type resins. Another object of the present invention is to provide a composite molded product of a three layer structure comprising nonolefin type resin layer/thermoplastic elastomer composition layer/crystalline olefin type resin layer, and a process for producing this molded product.

The thermoplastic elastomer composition according to one aspect of the present invention (aspect 1) comprises the following components (A) and (B).

Component (A): 5 to 95% by weight of a styrene type block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond unit.

Component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of polyester type thermoplastic elastomers, polyamide type thermoplastic elastomers, and polyurethane type thermoplastic elastomers.

The composite molded product according to another aspect of the present invention (aspect 2) comprises a thermoplastic resin layer (I) having a bending modulus of 2,000 to 60,000 kg/cm², comprising a crystalline olefin type resin or nonolefin type resin, and a thermoplastic elastomer layer (II) having a bending modulus of less than 2,000 kg/cm² and a JIS Shore hardness (A scale) according to JIS-K6301 of not more than 98, wherein said thermoplastic elastomer layer (II) comprises the following components (A) and (B).

Component (A): 5 to 95% by weight of a styrene type block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond unit.

Component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of polyester type thermoplastic elastomers, polyamide type thermoplastic elastomers, and polyurethane type thermoplastic elastomers.

The composite molded product according to still another aspect of the present invention (aspect 3) is a composite molded product in which one or more thermoplastic resin layers selected from aromatic polycarbonates, acrylic type resins and styrene type resins are laminated with a propylene

type resin layer through a thermoplastic elastomer composition layer (intermediate layer) comprising the following components (A) and (B).

Component (A): 5 to 95% by weight of a styrene type block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond unit.

Component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of polyester type thermoplastic elastomers, polyamide type thermoplastic elastomers, and polyurethane type thermoplastic elastomers.

The process for producing the composite molded product according to yet another aspect of the present invention (aspect 4) is a production process employing insert injection molding, double injection molding, or core back injection molding in which a thermoplastic resin having a bending modulus of 2,000 to 60,000 kg/cm² is molded first then a thermoplastic elastomer layer having a JIS Shore hardness (A scale) according to JIS-K6301 of not more than 98, and a bending modulus of below 2,000 kg/cm² is molded by injection molding process, characterized in that the thermoplastic elastomer layer basically contains a thermoplastic composition comprising the following components (A) and (B), and that the thermoplastic elastomer layer is fusion-bonded to the thermoplastic resin layer.

Component (A): 5 to 95% by weight of a styrene type block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond unit.

Component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of polyester type thermoplastic elastomers, polyamide type thermoplastic elastomers, and polyurethane type thermoplastic elastomers.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a composite injection molded product obtained in Example 11 of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[I] Thermoplastic elastomer composition

(1) Basic components of the thermoplastic elastomer composition

The physical properties of the thermoplastic elastomer according to the present invention are; a JIS Shore hardness (A Scale) according to JIS-K6301 of not more than 98, preferably 5 to 95, particularly preferably 10 to 90, bending modulus according to JIS-K7203 of below 2,000 kg/cm², preferably not more than 1,500 kg/cm², particularly preferably 0 to 1,000 kg/cm². Such thermoplastic elastomer composition is a composition containing as its basic components, a styrene type block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer

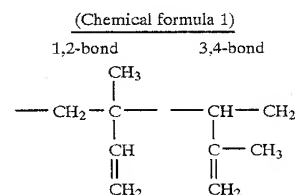
of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in the block (b) is not less than 40% of the total isoprene bond unit [hereinafter referred to as component (A)] and a specific thermoplastic elastomer [hereinafter referred to as component (B)].

<Component (A): Styrene type block copolymer>

The above-mentioned styrene type block copolymer is made of a block (a) comprising a polymer of styrene or a derivative thereof, and block (b) which is made of isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bond and the 3,4-bond in the isoprene polymer part in the block (b) is not less than 40%, preferably not less than 45%, particularly preferably not less than 50% of the total isoprene bond unit.

The polymer component constituting the above-mentioned block (a) is styrene or a derivative thereof and examples of the derivative of styrene include α -methylstyrene, 1-vinylnaphthalene, 2-vinylnaphthalene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 4-(phenylbutyl)styrene and the like. Among these, styrene and α -methylstyrene are preferable as the polymer component constituting the block (a).

The polymer or the copolymer constituting the above-mentioned block (b) is an isoprene homopolymer or a copolymer of isoprene and butadiene and the total amount of the 1,2 bond and the 3,4 bond in the isoprene polymer part shown below is not less than 40% (up to 100%) of the total isoprene bond unit and the isoprene/butadiene copolymer can be either random, block or tapered.



The isoprene bond units in the isoprene polymer part include 1,2-bond, 3,4-bond and 1,4-bond, but according to the present invention, by the selective use of those in which the amount of the 1,2-bond and that of the 3,4-bond is not less than 40% of the total isoprene bond unit, a styrene type block copolymer having excellent heat fusion properties can be obtained.

The ratio of the polymer block (a) comprising the styrene or a derivative thereof in the styrene type block copolymer of component (A) is preferably 5 to 50% by weight of said copolymer, more preferably 10 to 45% by weight. That is, the ratio of the block (b) comprising the above-mentioned isoprene homopolymer or the copolymer of isoprene and butadiene is 95 to 50% by weight, more preferably 90 to 55% by weight.

According to the present invention, it is more preferable to use a hydrogenated styrene type block copolymer for the component (A) of the composition. As for the hydrogenation degree, it is important to use a copolymer having an overall hydrogenation degree of not less than 95% by weight, preferably 97 to 100% by weight.

As for said styrene type block copolymer, it is preferable to use those having a weight average molecular weight of 50,000 to 500,000, preferably 60,000 to 400,000, particularly preferably 70,000 to 300,000.

The term "weight average molecular weight" means a weight average molecular weight measured by gel permeation chromatography (GPC) under the following conditions that is converted to a polystyrene basis.

(Conditions) Instrument: 150 C ALC/GPC (manufactured by Millipore Corp.)

Column: AD80M/S (manufactured by Showa Denko K.K.) three columns

Solvent: o-dichlorobenzene

Temperature: 140° C.

Rate of flow : 1 ml/min

inflow: 200 μ l

Concentration: 2 mg/ml (2,6-di-*t*-butyl-4-methylphenol was added as an antioxidant, in an amount of 0.2% by weight. The detection of the concentration was carried out at a wave length of 3.42 μ m, with MIRAN 1A, an infrared spectrophotometer manufactured by the FOXBORO COMPANY.)

Among the above-mentioned styrene type block copolymers, those having a weight average molecular weight exceeding 500,000 result in a poor moldability, and those having a weight average molecular weight below 50,000 provide poor rubber elasticity and poor mechanical strength. Those having a styrene content or a styrene derivative content of less than 5% by weight result in a poor mechanical strength, and those having a content exceeding 50% by weight provide poor flexibility. Those having a hydrogenation degree of below 95% by weight show inferior weather resistance and inferior heat resistance.

The styrene type block copolymer of the present invention can be obtained by the various methods shown below.

First, examples of a method for polymerizing the styrene type block copolymer include a method in which styrene or a derivative thereof, isoprene or isoprene-butadiene is polymerized sequentially using an alkyl lithium compound as the initiator, a method in which styrene or a derivative thereof is polymerized, then isoprene or a mixture of isoprene and butadiene is polymerized and then coupled by a coupling agent, or a method in which isoprene or an isoprene-butadiene mixture, then styrene or a derivative thereof are polymerized sequentially using a dilithium compound as the initiator. Examples of an alkyl lithium include an alkyl compound having 1-10 carbon atoms in the alkyl residual group, and particularly preferable examples include methyl lithium; ethyl lithium, pentyl lithium and butyl lithium. As the coupling agent, dichloromethane, dibromomethane, dichloroethane, dibromoethane, and dibromobenzene and the like can be used. Examples of the dilithium compound include naphthalene dilithium and dilithiohexylbenzene and the like. The amount of the compound used is decided depending on the desired molecular weight. However, 0.01 to 0.2 parts by weight of an initiator, 0.04 to 0.8 parts by weight of a coupling agent are generally used for 100 parts by weight of the total monomers used for the polymerization.

In order to assure that the total amount of the 1,2-bonds and the 3,4-bonds in the isoprene polymer part in the block (b) comprising isoprene homopolymer or a copolymer of isoprene and butadiene are not less than 40% of the total isoprene bond unit, a Lewis base is used as a co-catalyst in the polymerization of isoprene or isoprene-butadiene mixture. Examples of the Lewis base include ethers such as dimethyl ether, diethyl ether and tetrahydrofuran, glycol ethers such as ethylene glycol dimethyl ether and diethylene glycol dimethyl ether, and amine type compounds such as triethylamine, N,N,N',N'-tetramethylethylenediamine (TMEDA), and N-methylmorpholine. The amount of these Lewis bases used is generally 0.1 to 1000 times that of the lithium (in mole) of the polymerizing catalyst.

A solvent is preferably used for facilitating the control of the polymerization. As the solvent, an organic solvent which is inactive for the polymerization catalyst is used. Particularly preferable examples include aliphatic, alicyclic and aromatic hydrocarbons having 6 to 12 carbon atoms. Examples of such solvents include hexane, heptane, cyclohexane, methylcyclohexane, and benzene.

The polymerization is carried out in a temperature range of from 60 to 80° C. and in a time range of from 0.5 to 50 hours in any polymerization method.

The obtained styrene type block copolymer is subjected to hydrogenation treatment (hereinafter also simply referred to as hydrogenation) by known methods. In a preferable method, the copolymer is dissolved in a solvent which is inactive to the hydrogenation reaction and the hydrogenation catalyst then allowed to react with the molecular hydrogen by a known hydrogenation catalyst. Examples of the catalyst to be used include a heterogeneous catalyst comprising a support such as carbon, alumina and diatomaceous earth carrying Raney Nickel, or a metal such as Pt, Pd, Ru, Rh, and Ni, or Ziegler type catalyst comprising a transition metal and an alkyl aluminum compound, alkyl lithium compound and the like. The reaction is carried out at a hydrogen pressure of from normal to 200 kg/cm², a reaction temperature of from normal to 250° C., and the reaction time of from 0.1 to 100 hours.

The styrene type block copolymer after the reaction is obtained by solidifying the reaction mixture with methanol and the like followed by heating or drying under a reduced pressure, or by removing the solvent azeotropically by pouring the reaction mixture into boiling water, followed by heating or drying under reduced pressure.

<Component (B): Specific thermoplastic elastomer>

As the specific thermoplastic elastomer to be used for the thermoplastic elastomer composition of the present invention, one or more compounds selected from the group consisting of polyester type thermoplastic elastomers, polyamide type thermoplastic elastomers, and polyurethane type thermoplastic elastomers are used.

(i) Polyester type thermoplastic elastomer

As a polyester type elastomer, those having a bending modulus according to JIS K-7203 of not more than 10,000 kg/cm², particularly preferably not more than 5,000 kg/cm², and/or having a melting point by DSC (peak temperature) of not more than 230° C., particularly preferably not more than 220° C. are preferable. Such elastomers can be obtained by polycondensation of an oligomer obtained by esterification or ester exchange reaction of (1) an aliphatic and/or alicyclic diol having 2-12 carbon atoms, (2) an aromatic dicarboxylic acid or an alkyl ester thereof, and (3) a polyalkylene ether glycol having the weight average molecular weight of 400 to 6,000.

As the aliphatic and/or alicyclic diol having 2-12 carbon atoms used according to the present invention, a material known as raw materials for polyesters, particularly those known as raw materials for polyester elastomers can be used. Examples of such compounds include ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butanediol, 1,4-cyclohexane diol, 1,4-cyclohexane dimethanol and the like; a material mainly containing 1,4-butane diol or ethylene glycol is preferable, and particularly preferably used is a material mainly containing 1,4-butanediol. They can be used alone or in admixtures of two or more kinds.

As the aromatic dicarboxylic acid, those compounds known as a raw material for polyesters, particularly those for polyester elastomers can be used. Examples of such compounds include terephthalic acid, isophthalic acid, phthalic

acid, 2,6-naphthalene dicarboxylic acid and the like. A material mainly containing terephthalic acid and 2,6-naphthalene dicarboxylic acid is preferable, but particularly preferable is a material mainly containing terephthalic acid, and they can be used in admixtures of two or more kinds. Examples of an alkyl ester of the aromatic dicarboxylic acid include dimethyl esters such as dimethyl terephthalate, dimethyl isophthalate, dimethyl phthalate, 2,6-dimethyl naphthalate and a preferable example includes dimethyl terephthalate, 2,6-dimethyl naphthalate, and a particularly preferable example is dimethyl terephthalate. These can be used in admixtures of two or more kinds. In addition to the above-mentioned compounds, a diol having three functional groups, and other diols or other dicarboxylic acids and an ester thereof can be copolymerized in a small amount, and an aliphatic or alicyclic dicarboxylic acid such as adipic acid, or an alkyl ester thereof can be used as a copolymerizing component.

As the polyalkylene ether glycol, those having a weight average molecular weight of 400 to 6,000 are used, but a preferable weight average molecular weight is 500 to 4,000, and particularly preferable weight average molecular weight is 600 to 3,000. When the molecular weight is below 400, the resulting copolymer shows inferior block polymerization, and when the weight average molecular weight exceeds 6,000, the physical properties of the resulting polymer are degraded due to the phase separation in the system. Examples of the polyalkylene ether glycol include polyethylene glycol, poly(1,2 and 1,3 propylene ether) glycol, polytetramethylene ether glycol, polyhexamethylene ether glycol, a block or random copolymer of ethylene oxide and propylene oxide, a block or random copolymer of ethylene oxide and tetrahydrofuran, and the like. A particularly preferable example is polytetramethylene ether glycol.

The content of the polyalkylene ether glycol is desirably 5 to 95% by weight, preferably 10 to 85% by weight, particularly preferably 20 to 80% by weight of the resulting block copolymer. When the content is more than 95% by weight, it becomes difficult to give a polymer by condensation polymerization.

The polyester type copolymer according to the present invention can be (4) a polyester oligomer in which an aliphatic or alicyclic dicarboxylic acid and an aliphatic diol are condensed or (5) a polyester oligomer synthesized from an aliphatic lactone or an aliphatic monoalcohol carboxylic acid instead of (3) a polyalkylene ether glycol having a weight average molecular weight of 400 to 6,000.

An example of (4) includes a polyester oligomer having such a structure that one or more kinds of an alicyclic dicarboxylic acid such as 1,4-cyclohexane dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, dicyclohexyl-4,4'-dicarboxylic acid or an aliphatic dicarboxylic acid such as succinic acid, oxalic acid, adipic acid, and sebacic acid, is condensed with one or more kinds of diols such as ethylene glycol, propylene glycol, tetramethylene glycol, and pentamethylene glycol, and an example of (5) includes a polycaprolactone type polyester oligomer synthesized from ϵ -caprolactone and ω -oxycaproic acid and the like.

The esterification, ester exchange reaction, and polycondensation reaction of the present invention can be carried out according to ordinary methods. As a catalyst for these reactions, one or more known catalysts such as an alcoholate, chloride or oxide of tin, titanium, zinc, or manganese can be used respectively, however, an organic titanium type catalyst, particularly tetrabutyl titanate is desirable. As an assistant agents phosphoric acid, phosphorous acid, hypophosphorous acid, or a metal salt thereof can be

added as well. Particularly, addition of an alkali metal salt of hypophosphorous acid is preferable since the content of the terminal carboxyl group is decreased to improve the resistance to hydrolysis.

Examples of the alkali metal salt of the hypophosphorous acid include sodium hypophosphite, potassium hypophosphite, and lithium hypophosphite, and particularly desirable is sodium hypophosphite.

The amount of the alkali metal hypophosphite added is 1 to 1,000 ppm, preferably 3 to 200 ppm, more preferably 5 to 80 ppm to the resulting polymer. An amount of less than 1 ppm is not preferable since the effect of the addition cannot be fully obtained, and an amount of more than 1,000 ppm is not preferable either since the effect is not increased, but rather the polycondensation reaction is inhibited.

As for a method of addition, the alkali metal hypophosphite can be added to molten polymer in the form of a solution, slurry, or solid, and the timing of the addition is at least before the completion of the polycondensation reaction, that is, it can be added any time between before the esterification reaction or ester exchange reaction and before the completion of the polycondensation reaction. It is particularly preferable to add it in the form of a slurry just before the polycondensation under reduced pressure is started, since it causes less degradation of the polymerization property.

In the reaction step, another additive may also be present. For example, a hindered phenol type antioxidant, hindered amine type antioxidant, phosphorus type antioxidant, sulphur type antioxidant, triazole type light stabilizer, and other known additives can be used. According to the present invention, it is particularly preferable to add a hindered phenol type antioxidant in an amount of 0.01 to 1% by weight to the polymer, from the view point of the resulting effects. Esterification or ester exchange reaction is carried out normally at 120 to 250° C., preferably 150 to 230° C., and the melt polycondensation reaction is carried out under reduced pressure of usually not more than 10 torr, at 200 to 280° C. for 2 to 6 hours.

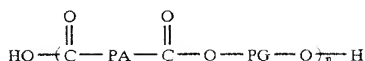
Usually, the polymer obtained by melt polymerization is kept at a temperature not less than the melting point and sequentially discharged from the reaction vessel and pelletized. The obtained pellets can be subjected to solid phase polymerization if necessary.

The bending modulus of such polyester type elastomer according to JIS K-7203 is preferably not more than 10,000 kg/cm², particularly preferably not more than 5,000 kg/cm². The melting point (peak temperature) of the polyester elastomer obtained according to DSC (Differential Scanning Calorimetry) is preferably not more than 230° C., particularly preferably not more than 220° C.

Such polyester type elastomers include commercially available polymers "PELPRENE P" or "PELPRENE S" (commercial names, available from Toyobo Co., Ltd.) or "HYTREL" (commercial name, available from Toray-Du Pont Industries, Inc.), "LOMOD" (commercial name, available from Nippon G.E. Plastic Co., Ltd.), "FLECMER" (commercial name, available from The Nippon Synthetic Chemical Industry, Co., Ltd.), "Teijin Polyester Elastomer" (commercial name, available from Teijin Ltd.) and the like.

(ii) Polyamide type thermoplastic elastomer

The polyamide type thermoplastic elastomer contains a polyamide (Nylon 6, Nylon 66, Nylon 11, Nylon 12 and the like) as a hard segment and a polyether or polyester as a soft segment. For example, the polyether block amide can be represented by the following general formula (I):



(wherein PA represents the block of a polyamide constituting a hard segment, and PG represents the block of a polyether constituting a soft segment.)

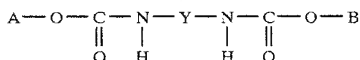
The polyether block amide which is used in the present invention and which can be represented by the above-mentioned general formula (I) itself is a known substance as it is disclosed in the specification of U.S. Pat. No. 3,044,978 and the like.

This substance can be prepared by polycondensation of the components (i) a diamine and a dicarboxylate, lactames or an amino dicarboxylic acid (PA component), (ii) a polyoxyalkylene glycol such as polyoxyethylene glycol, polyoxypropylene glycol (PG component) and (iii) a dicarboxylic acid.

The commercially available products include "PEBAX" (commercial name, available from Toray Industries, Inc.), "DAIAMID-PAE" (commercial name, available from Daicel-Hüls Co., Ltd.), "UBE Polyamide Elastomer" (commercial name, available from Ube Industries, Ltd.), "NOVAMID PAE" (commercial name, available from Mitsubishi Chemical Corp.), "GRILUX A" (commercial name, available from Dainippon Ink and Chemicals, Inc.), "GRILON ELX, ELY" (commercial name, available from MS Japan Co., Ltd.) and the like.

(iii) Polyurethane type thermoplastic elastomer

The polyurethane type thermoplastic elastomer contains a hard segment comprising a diisocyanate and a short chain glycol (ethylene glycol, propylene glycol, 1,4-butanediol, bisphenol A and the like), and a soft segment comprising a diisocyanate and a long chain polyol. The long-chain polyol includes those of a polyether type such as poly(alkylene oxide) glycol having a molecular weight of 400 to 6,000 (for example, polyethylene glycol, poly(1,2 and 1,3 propylene oxide) glycol, poly(tetramethylene oxide) glycol, poly(hexamethylene oxide) glycol and the like), or those of polyester type such as polyalkylene adipate, polycaprolactone, and polycarbonate. Such polyurethane type thermoplastic elastomer is a compound having the structure represented by the following general formula (II).



(wherein A represents a hard segment comprising a diisocyanate and a short-chain glycol, B represents a soft segment comprising a diisocyanate and a long-chain polyol, Y represents the residual group of the diisocyanate compound of the urethane bond linking the A segment and B segment.)

As the diisocyanate compound, a known and normally used compound such as phenylene diisocyanate, tolylene diisocyanate, xylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate and the like can be used.

Examples of the commercially available polyurethane type thermoplastic elastomer include "ELASTOLLAN" (commercial name, available from Takeda Badische Urethane Ind.), "MIRACTRAN" (commercial name, available from Nippon Miractran Co., Ltd), "LEZAMIN" (commercial name, available from Dainichiseika Colour &

Chemicals Mfg. Co., Ltd.) and "Y-Fine P" (commercial name, available from Asahi Glass Co., Ltd.) and the like.

Among those thermoplastic elastomers, a polyester type thermoplastic elastomer is preferable due to its good compatibility with the component (A).

(2) Additional compounding materials

In addition to the basic components (A) and (B), any of compounding components can be added to the thermoplastic elastomer of the present invention for various purposes.

Illustratively, additives such as antioxidants, thermal stabilizers, light stabilizers, UV absorbers, neutralizing agents, lubricants, anti-fogging agents, antiblocking agents, slipping agents, crosslinking agents, crosslinking assistants, coloring agents, flame-retardants, dispersing agents, anti-static agents can be added. Among these, it is particularly important to add an antioxidant, and one or more antioxidants selected from phenol types, phosphite types and thioether types can be used.

It is also possible to blend an additional compounding material including other thermoplastic resins except for the above-mentioned components (A) and (B), or various elastomers, various plasticizers, and various fillers and the like in a range that does not notably mar the effect of the present invention.

Examples of thermoplastic resins as the additional compounding component include olefin type resins such as a propylene type resin, ethylene type resin, and polybutene-1 resin, styrene type resins such as polystyrene, acrylonitrile-styrene copolymer, and acrylonitrile-butadiene-styrene copolymer, polyamide type resins such as a polyphenylene ether type resin, Nylon 6, and Nylon 66, polyester type resins such as polyethylene terephthalate and polybutylene terephthalate, polyoxy methylene type resins such as polyoxymethylene homopolymer and polyoxymethylene copolymer, and polymethyl methacrylate type resins etc.

The above-mentioned propylene type resins are propylene homopolymers and copolymers wherein the main component is propylene, and illustrative examples include propylene/ethylene random copolymers, propylene/ethylene block copolymers and the like.

Examples of the above-mentioned ethylene type resins include polyethylene resins, ethylene/ α -olefin copolymers, ethylene/vinyl acetate copolymers, ethylene(meth)acrylic acid copolymers, ethylene (meth)acrylic ester copolymers and the like.

As the above-mentioned polyethylene resin, a low density polyethylene resin produced by high-pressure process according to an ordinary method, or a copolymer of ethylene and olefin having crystallinity as measured by X ray diffraction method of 30 to 95%, which is obtained by a medium- or low-pressure process can be used.

Examples of the straight-chain α -olefin, which is the above-mentioned comonomer, include butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1 and the like. These can be used in admixtures of two or more kinds.

The thermoplastic resin can be used alone, or in admixtures of two or more kinds.

Examples of the various elastomers include ethylene type elastomers such as ethylene/propylene binary copolymer (EPM), ethylene/propylene/nonconjugate diene ternary copolymer rubber (EPDM), ethylene/butene-1 binary copolymer rubber (EBM), ethylene/propylene/butene-1 ternary copolymer rubber, ethylene/hexene copolymer, ethylene/octene copolymer which is a polymer having non-crystallinity or low crystallinity of below 30%. The elastomer can be used alone or in admixtures of two or more kinds.

In order to further increase the compatibility between the components (A) and (B) used for the thermoplastic elastomer layer, and to increase the bonding strength with the olefin type resin or the nonolefin type resin, a compatibilizer such as a maleated polyolefin including maleated polypropylene, and maleated polyethylene, or maleated SEBS, maleated SEPS, and a hydrogenated product of maleated styrene/conjugate diene block copolymer such as maleated hydrogenated styrene/butadiene/isoprene/styrene copolymer can be compounded as well.

Examples of the above-mentioned inorganic filler include talc, calcium carbonate, mica, glass fiber, glass balloon, carbon fiber and the like.

Examples of the plasticizer used as an additional component according to the present invention include a softening agent for a hydrocarbon type rubber having a weight average molecular weight of 300 to 3,000 and polybutene.

The softening agent for the hydrocarbon type rubber is generally a mixture of an aromatic ring, naphthene ring and paraffin ring, and those in which the carbon number in the paraffin chain shares 50% or more of the total carbon are called paraffin type oils, those in which the carbon in the naphthene ring shares 30 to 45% are called naphthene type oil and those having aromatic carbons in an amount of more than 30% are called aromatic type oils. Among these, a paraffin type oil is preferably used from the view point of weather resistance.

(3) Compounding ratio

The compounding ratio of each component constituting the thermoplastic elastomer of the composite molded product according to the present invention is that Component (A) is 5 to 95% by weight, preferably 10 to 90% by weight, particularly preferably 20 to 80% by weight of the total of component (A) and component (B).

When the compounding ratio of the component (A) is below 5% by weight, the heat fusion property of the resulting thermoplastic elastomer layer to the olefin type resin layer becomes inferior, and when it exceeds 95% by weight, the fusion bonding property to the nonolefin type resin layer becomes inferior.

The amount of the component (B) is 95 to 5% by weight, preferably 90 to 10% by weight, particularly preferably 80 to 20% by weight of the total of component (A) and component (B).

When the compounding ratio of the component (B) exceeds 95% by weight, the heat fusion property of the thermoplastic elastomer layer to the olefin type resin layer becomes inferior, while an amount of below 5% by weight results in an inferior heat fusion property to the nonolefin type resin layer.

[II] Composite molded product

In the composite molded product according to the present invention, a thermoplastic elastomer layer and a thermoplastic resin (crystalline olefin type resin or nonolefin type resin) layer are bonded by means of fusion bonding.

The layer structure includes a two layer structure comprising a thermoplastic elastomer layer and a thermoplastic resin layer, a three layer structure comprising a thermoplastic resin layer/a thermoplastic elastomer layer/a thermoplastic resin layer, having the thermoplastic elastomer as the intermediate layer, and a multilayer structure wherein these structures are combined.

(1) Thermoplastic elastomer layer (II)

This contains the above-described thermoplastic elastomer composition of the present invention as the base material.

(2) Thermoplastic resin layer (I)

The thermoplastic resin used for the other layer of the composite molded product of the present invention (hereinafter also referred to simply as "resin layer") includes a crystalline olefin type resin and a nonolefin type resin.

(i) Crystalline olefin type resin

The crystalline olefin type resin is one or more resins selected from the group consisting of a propylene type resin, ethylene type resin, crystalline butene-1- resin. Preferably it is a propylene type resin having a bending modulus according to JIS-K7203 of 2,000 to 60,000 kg/cm², preferably 3,000 to 60,000 kg/cm², particularly preferably 4,000 to 60,000 kg/cm².

(a) Propylene type resin

The above-mentioned propylene type resin includes propylene homopolymers, copolymer resins containing propylene as a main component, such as propylene/ethylene random copolymers and propylene/ethylene block copolymers. The polypropylene resin has a melt flow rate (JIS-K6758, 230° C., 2.16 kg load) of 0.01 to 100 g/10 min, preferably 0.05 to 80 g/10 min, particularly preferably 0.1 to 60 g/10 min. In the preferable propylene/ethylene random copolymer or propylene/ethylene block copolymer, the ethylene content is 0.01 to 15% by weight, preferably 0.1 to 13% by weight, particularly preferably 1 to 10% by weight. The ethylene content referred to here is a value measured by IR spectral analysis and the like.

(b) Ethylene type resin

The above-mentioned ethylene type resin is a polyethylene resin having a melt flow rate (190° C., 2.16 kg load) of 0.01 to 100 g/10 min, preferably 0.01 to 50 g/10 min, which is produced by an ordinary method.

Such polyethylene resin includes a low density polyethylene resin (branched polyethylene resin) produced by high-pressure process, an ethylene homopolymer produced by medium- or low-pressure process, or a low density, medium density and high density polyethylene resin (straight-chain polyethylene resin) which is a copolymer of ethylene and olefin.

Examples of the α -olefin, which is the above-mentioned comonomer, include butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1 and the like, and these can be used in admixture of two or more kinds.

As illustrative production conditions, generally a copolymerization of ethylene and α -olefin is carried out using a Ziegler type catalyst, vanadium type catalyst, Kaminsky type (metallocene type) catalyst and the like, at a pressure of 5 to 2,500 kg/cm², and temperature of 50 to 300° C. For example a method described in Japanese Patent Publication No. 56-18132 and the like is known.

Among these, particularly preferable resins are a straight-chain polyethylene resin obtained by a medium- or low-pressure process.

(c) Crystalline butene-1 resin

As the above-mentioned crystalline butene-1 resin, a crystalline resin synthesized from butene-1 monomer which may contain a small amount (not more than 20% by weight) of another comonomer such as ethylene and propylene, having a density of 0.890 to 0.925 g/cm³, preferably 0.893 to 0.923 g/cm³, particularly preferably 0.900 to 0.920 g/cm³, a melt flow rate (at 190° C., 2.16 kg load) of 0.01 to 1,000 g/10 min, preferably 0.05 to 500 g/10 min, particularly preferably 0.1 to 100 g/10 min, a weight average molecular weight of 100,000 to 3,000,000, preferably 50,000 to 2,500,000 is preferably used.

(ii) Nonolefin type resin

A nonolefin type resin is one or more resins selected from the group consisting of a nonolefin type resin such as an

aromatic polycarbonate, an acrylic type resin, a styrene type resin, polyvinyl chloride, and a modified polyphenylene ether, and preferable examples include an aromatic polycarbonate, acrylic type resin, styrene type resin, having a bending modulus according to JIS-K7203 of not less than 15,000 kg/cm², preferably 18,000 to 60,000 kg/cm².

(a) Aromatic polycarbonate

The above-mentioned aromatic polycarbonate is produced by carrying out a reaction between an aromatic hydroxy compound, optionally together with a small amount of a polyhydroxy compound, and phosgene. The aromatic dihydroxy compound optionally with a small amount of polyhydroxy compound can also be subjected to ester exchange reaction with a diester carbonate to produce the aromatic polycarbonate. If necessary, a trifunctional compound or a compound having higher functionality, as a branching agent, or a molecular weight controlling agent are supplied to the reaction. The aromatic polycarbonate resin is a branched or unbranched thermoplastic aromatic polycarbonate resin.

Examples of the aromatic dihydroxy compound include 2,2-bis(4-hydroxyphenyl)propane (hereinafter also simply referred to as "bisphenol A"), tetramethyl bisphenol A, tetrabromobisphenol A, bis(4-hydroxyphenyl)-p-isopropylbenzene, hydroquinone, resocinol, 4,4'-dihydroxyphenyl, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulphone, bis(4-hydroxyphenyl)sulphoxide, bis(4-hydroxyphenyl)sulphide, bis(4-hydroxyphenyl)ketone, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)cyclohexane and the like with bisphenol A particularly preferable.

In order to obtain a branched aromatic polycarbonate resin, a polyhydroxy compound represented by phloroglucine, 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-2,4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptane, 2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-3,2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptane, 1,3,5-tri(4-hydroxyphenyl)benzene, 1,1,1-tri(4-hydroxyphenyl)ethane and the like, and 3,3-bis(4-hydroxyphenyl)oxyindole [=isatin (bisphenol A)], 5-chloroisatin, 5,7-dichloroisatin, 5-bromoisatin and the like is used to replace a part (for example 0.1 to 2 mol %) of the above-mentioned dihydroxy compound.

The monovalent aromatic hydroxy compound which is suitable for controlling the molecular weight includes m- and p-methyl phenol, m- and p-propyl phenol, p-bromophenol, p-tertbutylphenol and p-long chain alkyl substituted phenol and the like. Preferable aromatic polycarbonate resins include bis(4-hydroxyphenyl)alkane type compounds, and particularly preferable is a polycarbonate whose main raw material is bisphenol A. A polycarbonate copolymer obtained from two or more kinds of aromatic dihydroxy compounds, a branched polycarbonate resin obtained by using a small amount of tri-valent phenol type compound are preferable examples as well (Japanese Patent Laid-open Nos. 63-30524 and 56-55328, Japanese Patent Publication Nos. 55-414, 60-25049 and 3-49930). The aromatic polycarbonate resin can be used in admixtures of two or more kinds.

The weight average molecular weight of a preferable polycarbonate resin measured by GPC and converted to polystyrene basis is in the range of from 10,000 to 150,000, preferably from 15,000 to 100,000, and most preferably from 350,000 to 80,000, from the view point of well balanced heat resistance, mechanical strength and molding processability and the like.

Commercially available examples include "IUPILON" (commercial name, available from Mitsubishi Engineering

Plastics Co., Ltd.), and "NOVAREX" (commercial name, available from Mitsubishi Engineering Plastics Co., Ltd.) and the like.

(b) Acrylic type resin

The acrylic type resin is a resin obtained by polymerization of acrylic acid and a derivative thereof, illustrative examples include polymers and copolymers of acrylic acid, acrylic ester, acrylamide, acrylonitrile, methacrylic acid, methacrylic ester and the like. Preferable examples are a polymer of methacrylic ester such as methyl methacrylate and ethyl methacrylate and particularly preferable is a polymer of methyl methacrylate (polymethyl methacrylate resin). Commercially available products include "ACRY-PET" (commercial name, available from Mitsubishi Rayon Co., Ltd.) and the like.

(c) Styrene type resin

The above-mentioned styrene type resin includes polystyrene made of styrene homopolymer (GP polystyrene; commercially available from Mitsubishi Chemical Co., Ltd. under the commercial name of "DIAREX" and the like), high impact polystyrene (commercially available from Mitsubishi Chemical Corp. under the commercial name of "DIAREX" and the like), ABS resin (acrylonitrile/butadiene/styrene resin) (commercially available from Mitsubishi Chemical Corp. under the commercial name of "TUFREX" and the like), AS resin (acrylonitrile/styrene resin), (commercially available from Mitsubishi Chemical Corp. under the commercial name of "SANREX" and the like.)

The ABS resin is produced by emulsion polymerization, mass-suspension polymerization or mass polymerization, has a composition comprising 10 to 30% by weight of acrylonitrile, 5 to 45% by weight of butadiene, and 50 to 85% by weight of styrene and includes a polymer wherein a-methyl styrene is used instead of styrene.

(d) Polyvinyl chloride

The above-mentioned polyvinyl chloride is a compound resin whose basic component is a polymer obtained by polymerization of vinyl chloride and preferably it is a rigid PVC compound resin. Commercially available products include "VINIKA COMPOUND" (commercial name, available from Mitsubishi Chemical MKV Co., Ltd.) and the like.

(e) Modified polyphenylene ether

The above-mentioned modified polyphenylene ether is an alloy of a polyphenylene ether which is an amorphous highly heat resistant resin and a crystalline highly heat resistant resin including a polyamide resin, polyester resin such as polybutylene terephthalate, propylene type resin, and shock resisting polystyrene and the like. Commercially available products include "IUPIACE" (commercial name, available from Mitsubishi Chemical Engineering Plastics Co., Ltd.), "LEMALLOY" (commercial name, available from Mitsubishi Chemical Co., Ltd.) and the like.

Polyphenylene ether alone, which is not alloyed with the crystalline highly heat resistant resin, is not practical since the molding can be done only at a high temperature and the molding processability is inferior.

(iii) Additional compounding agent

These resins can be compounded with various other additives including fillers such as rubber components, talc, calcium carbonate, mica and glass fiber, plasticizers such as paraffin oil, antioxidants, heat stabilizers, light stabilizers, UV absorbing agents, neutralizing agents, slip additives, compatibilizers, lubricants, anti-fogging agents, anti-blocking agents, slipping agents, dispersing agents, coloring agents, antibacterial agents, and fluorescent whiteners.

15

[III] Production of a composite molded body

Examples of a method of producing such a composite molded body include various molding methods such as extrusion lamination molding method, co-extrusion molding method, blow molding method, insert injection molding method, double injection molding method, core back injection molding method, sandwich injection molding method, and injection press molding method.

Among the above-mentioned molding methods, insert injection molding method is a process in which a core material (a resin for a resin layer) is molded by injection molding, extrusion molding, sheet molding, or a film molding process and the molded product is inserted into a die then a surface material (a thermoplastic elastomer) is injected into the gap between the molded product and the dies and molded, or a surface material (a thermoplastic elastomer) is previously molded by injection molding, extrusion molding, sheet molding or film molding, and the molded product is inserted into a die and a core material (a resin for a resin layer) is injected into the gap between the molded product and the dies and molded.

The double injection molding method is a molding process in which a core material (a resin for a resin layer) is subjected to injection molding using two or more injection molding machines and the dies are rotated or transferred so that the cavity of the dies is replaced to provide a gap between the molded product and the dies, and a surface material (a thermoplastic elastomer) is injected thereinto and molded.

The core back injection molding method is a process in which a core material (a resin for a resin layer) is molded using one injection molding machine and one die, then the cavity capacity of the die is increased and a surface material (a thermoplastic elastomer) is injected into the gap between the molded product and the die and molded.

The molding of the core material can be carried out by an ordinary injection molding method or by gas injection molding method.

As the injection molding conditions for the core material, a molding temperature of generally 100 to 300° C., preferably 150 to 280° C. is employed and an injection pressure of 50 to 1,000 kg/cm², preferably 100 to 800 kg/cm² is employed.

Further, it is important that the average thickness of the core material layer of the injection molded product be 0.5 to 6 mm, and those exceeding the above range cause shrink marks on the core material layer and the surface of the molded product shows inferior smoothness. Also those below the range may not be able to satisfy the mechanical properties such as rigidity, and strength, heat resistance and durability that are required for automobile interior parts.

It is important that the average thickness of the surface material layer be 1 to 5 mm, those exceeding the above range providing poor soft-feeling, while those below the range provide poor adhesive force between the core material and the surface material.

As the injection molding conditions for the surface material layer, a molding temperature of generally 150 to 300° C., preferably 200 to 290° C., and particularly preferably 220 to 280° C., an injection pressure of 50 to 1,000 kg/cm² and preferably 100 to 800 kg/cm² are employed.

16

Runners or spools comprising only the surface material can be recycled for the surface material, and runners or spools comprising only the core material or a core material and the surface material can be recycled for the core material and defective molded products and the like can be recycled for the core material as well.

[IV] Uses

The composite molded product comprising the thermoplastic elastomer layer and the resin layer thus obtained can be used for various industrial parts.

Illustratively, they can be used for automobile interior parts such as instrument panels, center panels, center console boxes, door trim, pillars, assist grips, steering wheel, air bag covers, and automobile exterior parts such as molling, automobile functional parts such as rack and pinion boots, suspension covers, CVJ boots, electric appliance parts such as vacuum cleaner bumpers, remote control switches, and various key top and the like for OA devices, products for underwater use such as water goggles, underwater covers for cameras, and various covering parts, and industrial parts having various packing for imparting hermetic, water proofing, sound proofing, and damping properties and the like, and electric, electronic parts such as curl cord wire coating, belts, hoses, tubes and sound deadening gear, sports goods and the like.

EXAMPLES

The present invention will be further described by the following examples.

[I] Evaluation method

Various evaluations were carried out in these examples and comparative examples according to the following testing methods.

For producing the test sample, a core material layer (a thermoplastic resin layer) was first molded using a double injection molding machine (KS-2C-680 manufactured by Takahashi Seiki Kogyojo K.K.). Then a surface material layer (a thermoplastic elastomer layer) was molded at 240° C. to give a composite injection molded product of 300 mm×300 mm×4 mm (both the core material layer and the surface material layers having a thickness of 2 mm).

(1) JIS Shore hardness: A scale [-]. Based on JIS-K6301

(2) Heat fusion property (peel strength)

A strip specimen cut out from the above-mentioned composite injection molded product having a width of 25 mm, a length of 100 mm, a thickness of 4 mm (both the core material layer and the surface material layer had a thickness of 2 mm) was used and the surface material layer and the core material layer were pulled in the opposite directions at a rate of 200 mm/min and the peel strength of the bonded interface between the surface material layer and the core material layer was measured.

[II] Raw materials

(1) Thermoplastic elastomer layer [surface material], Tables 1 and 2.

TABLE 1

Component (A)				
Block Copolymer	Amount (%) of 1,2-bond and 3,4-bond in isoprene polymer segment	Weight average molecular weight	Styrene content (wt %)	Hardness (JIS-A)
A-1 ^{*1}	55	99,000	20	57
A-2 ^{*2}	70	85,000	20	68
A-3 ^{*3}	55	99,000	20	52
A-4 ^{*4}	8	73,000	30	80
A-5 ^{*5}	—	86,000	29	75

^{*1}Styrene/isoprene/styrene block copolymer ("HYBRAR-VS-3" produced by Kuraray Co., LTD.)

^{*2}Styrene/isoprene/styrene block copolymer ("HYBRAR-VS-1" produced by Kuraray Co., LTD.)

^{*3}Hydrogenated product of A-1 ("HYBRAR-HVS-3" produced by Kuraray Co., LTD.)

^{*4}Hydrogenated product of styrene/isoprene/styrene block copolymer ("SEPTON2007P" produced by Kuraray Co., LTD.)

^{*5}Hydrogenated product of styrene/butadiene/styrene block copolymer ("KRATON G1652" produced by Shell Chemical Co.)

TABLE 2

Component (B)						
Thermoplastic elastomer	Type	Producer Trade name	Grade name	Hardness (JIS-A)	Modulus in flexure kg/cm ²	Melting point (peak temp.) °C.
B-1	Polyester	Toyobo Co. "PELPRENE"	P30B	71	150	160
B-2	Polyester	Toyobo Co. "PELPRENE"	P90B	96	1650	203
B-3	Polyamide	Toray Industries "PEBAX"	2533SAOO	75	—	—
B-4	Polyurethane	Takeda-Badische Urethane Ind. "ELASTOLLAN"	ET-265R	65	—	—
B-5	Styrene	Mitsubishi Chemical Corp. "RABALON"	MJ7300C	75	—	—
B-6	Olefin	Mitsubishi Chemical Corp. "THERMORUN"	T3551B	55	—	—

(2) Thermoplastic resin layer [core material]

PP (crystalline polypropylene resin): "Mitsubishi Polypro BC03B" available from Mitsubishi Chemical Corp. (bending modulus of 12,000 kg/cm²)

PC (polycarbonate resin): "NOVAREX 7027A" available from Mitsubishi Chemical Corp. (bending modulus of 22,500 kg/cm²)

ABS (acrylonitrile/butadiene/styrene resin): "TUFREX TFX-410" available from Mitsubishi Chemical Corp. (bending modulus of 26,000 kg/cm²)

PMMA (polymethylmethacrylate resin): "ACRYPET IR H-70" available from Mitsubishi Rayon Co., Ltd. (bending modulus of 13,000 kg/cm²)

[III] Examples and Comparative Examples

Examples 1 to 10 and Comparative examples 1 to 8

The components were compounded according to the compositions (parts by weight) shown in Tables 3 to 4 and a phenol type antioxidant (available from Ciba-Geigy Co., Ltd., under the commercial name of "IRGANOX 1010") was further added therewith in an amount of 0.2 parts by weight to 100 parts by weight of the total amount of the composition, then melt kneading was carried out at a set temperature of 240° C. by a double-screw extruder having a cylinder diameter of 45 mm, a compression ratio L/D=33, to obtain an extruded product in the form of a strand, which was then cut into pellets. The obtained TPE composition pellets were made into a sheet by injection molding as described above and the sheet was subjected to the above-mentioned evaluations. The results of these evaluations are shown in Tables 3 and 4.

TABLE 3

	Example									
	1	2	3	4	5	6	7	8	9	10
Material of surface layer:										
Composition (part by weight):										
Component (A)										
A-1	50	—	—	—	—	—	—	—	—	—
A-2	—	50	—	—	—	—	—	—	—	—
A-3	—	—	50	50	50	50	70	30	25	25

TABLE 3-continued

	Example									
	1	2	3	4	5	6	7	8	9	10
Component (B)										
B-1	50	50	50	—	—	—	30	70	50	50
B-2	—	—	—	50	—	—	—	—	—	—
B-3	—	—	—	—	50	—	—	—	—	—
B-4	—	—	—	—	—	50	—	—	—	—
B-5	—	—	—	—	—	—	—	—	25	—
B-6	—	—	—	—	—	—	—	—	—	25
Properties:										
Hardness (JIS-A)	68	67	68	89	69	65	69	74	75	65
Bending modulus (kg/cm ²)	100	100	100	500	120	—	120	140	150	—
Evaluation:										
Heating fusing property (Peeling strength: kg/25 mm)										
Core material										
PP	4.1	4.0	4.4	6.6	3.7	3.5	4.5	2.2	1.1	1.9
PC	6.6	6.4	7.1	10.7	6.4	5.7	1.3	18.9	8.8	8.3
ABS	6.0	5.9	6.5	9.8	6.4	5.2	1.3	6.8	6.8	8.9
PMMA	8.0	7.9	8.8	13.2	2.1	7.0	1.4	8.5	7.9	9.0

25

TABLE 4

	Comparative Example							
	1	2	3	4	5	6	7	8
Material of surface layer:								
Composition (part by weight):								
Component (A)								
A-1	—	—	—	—	—	—	—	—
A-2	—	—	—	—	—	—	—	—
A-3	100	—	—	—	50	50	—	—
A-4	—	—	—	—	—	—	50	—
A-5	—	—	—	—	—	—	—	50
Component (B)								
B-1	—	100	—	—	—	—	50	50
B-2	—	—	—	—	—	—	—	—
B-3	—	—	—	—	—	—	—	—
B-4	—	—	—	—	—	—	—	—
B-5	—	—	100	—	50	—	—	—
B-6	—	—	—	100	—	50	—	—
Properties:								
Hardness (JIS-A)	52	71	75	55	62	45	80	77
Bending modulus (kg/cm ²)	—	150	150	—	—	—	290	250
Evaluation:								
Heat fusing property (Peeling strength: kg/25 mm)								
Core material								
PP	4.7	X	6.4	5.8	5.9	5.3	X	X
PC	X	20.0	X	X	X	X	3.2	6.0
ABS	X	7.4	X	X	X	X	2.6	4.2
PMMA	X	9.4	X	X	X	X	4.0	7.4

Note

X: <0.1 kg/25 mm, Range of no practical use

EXAMPLE 11

A crystalline polyolefin type resin (crystalline polypropylene resin) available from Mitsubishi Chemical Corp. under the commercial name of "MITSUBISHI POLYPRO BC03B" (bending modulus of 12,000 kg/cm²) and a non-polyolefin type resin (polycarbonate resin), available from Mitsubishi Chemical Corp. under the commercial name of "NOVAREX 7027A" (bending modulus of 22,500 kg/cm²) were subjected to injection molding by an inline screw type injection molding machine (IS90B, a small type injection molding machine manufactured by Toshiba Machine Co., Ltd.,) and a sheet of 120 mm×120 mm×2 mm was obtained, then it was cut to a size of 120 mm×60 mm×2 mm and these two sheets were juxtaposed as shown in FIG. 1, and inserted into a mold for a sheet of 120 mm×120 mm×4 mm. Then the thermoplastic elastomer composition of Example 4 was injected into the gap between the molded sheets and the mold using an inline screw type injection molding machine (IS90B, a small type injection molding machine manufactured by Toshiba Machine Co., Ltd.,) at an injection pressure of 500 kg/cm², injection temperature of 240° C., and mold temperature of 40° C., to give a composite injection molded product wherein the thermoplastic elastomer composition part had a size of 120 mm×120 mm×2 mm.

The merits of the thermoplastic elastomer composition according to the present invention and the composite molded product having such elastomer composition as one of the layers are that they show excellent fusion bonding properties and high peeling strength to wards both crystalline polyolefin type and nonpolyolefin type thermoplastic resins.

In particular, when one or more resins selected from polycarbonate and an acrylic type resin are used as the thermoplastic resin layer, the thermoplastic elastomer comprising a styrene type block copolymer as component (A) and a polyester type thermoplastic elastomer selected as component (B) shows particularly high heat fusion properties towards the thermoplastic resin layer.

What is claimed is:

1. A thermoplastic elastomer composition, comprising the following components (A) and (B);

component (A) 5 to 95% by weight of a hydrogenated product of a block copolymer comprising block (a)

- which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bonds and the 3,4-bonds in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond units;
- component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting thermoplastic polyester elastomers thermoplastic polyamide elastomers, and thermoplastic polyurethane elastomers, wherein said component (B) has a JIS Shore hardness (A Scale) of not more than 96 according to JIS-K6301, wherein said hydrogenated product has a hydrogenation degree of not less than 95% by weight.
2. A thermoplastic elastomer composition according to claim 1, wherein the total amount of the 1,2-bonds and the 3,4-bonds in the isoprene polymer part in said block (b) is not less than 45% of the total isoprene bonds units.
3. A thermoplastic elastomer composition according to claim 1, wherein the ratio of said block (a) in said component (A) is 10 to 45% by weight, and the ratio of said block (b) in said component (A) is 90 to 55% by weight.
4. A thermoplastic elastomer composition according to claim 1, wherein said component (B) is a thermoplastic polyester elastomer which has a bending modulus (according to JIS K-7203) of not more than 10,000, and a melting point by DSC (peak temperature) of not more than 230° C.
5. A thermoplastic elastomer composition according to claim 1, wherein said component (B) is a thermoplastic polyester elastomer which is an elastomer obtained by polycondensation of an aliphatic and/or alicyclic diol having 2 to 12 carbon atoms, an aromatic dicarboxylic acid or an alkyl ester thereof, and a polyalkylene ether glycol.
6. A thermoplastic elastomer composition according to claim 1, wherein said component (B) is a thermoplastic polyurethane elastomer which is an elastomer made of a hard segment block comprising a diisocyanate and a short-chain glycol, and a soft segment block comprising a diisocyanate and a long-chain polyol.
7. A thermoplastic elastomer composition according to claim 1, which contains said component (A) in an amount of 20 to 80% by weight and said component (B) in an amount of 80 to 20% by weight.
8. A thermoplastic elastomer composition according to claim 1, wherein said component (B) is a thermoplastic

polyamide elastomer which is an elastomer made of a hard segment block comprising a polyamide and a soft segment block comprising a polyether or polyester.

9. A thermoplastic elastomer composition comprising the following components (A) and (B):

component (A): 5 to 95% by weight of a block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bonds and the 3,4-bonds in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond units;

component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of thermoplastic polyester elastomers, thermoplastic polyamide elastomers, and thermoplastic polyurethane elastomers, wherein said composition has a^a ending modulus according to JIS-K7203 of 0 to 1,000 kg/cm².

10. A thermoplastic elastomer composition comprising the following components (A) and (B);

component (A): 5 to 95% by weight of a block copolymer or a hydrogenated product thereof, comprising block (a) which is made of a polymer of styrene or a derivative thereof, and block (b) which is made of an isoprene homopolymer or a copolymer of isoprene and butadiene, wherein the total amount of the 1,2-bonds and the 3,4-bonds in the isoprene polymer part in block (b) is not less than 40% of the total isoprene bond units;

component (B): 95 to 5% by weight of one or more thermoplastic elastomers which are selected from the group consisting of thermoplastic polyester elastomers, thermoplastic polyamide elastomers, and thermoplastic polyurethane elastomers, wherein said component (B) has a JIS Shore hardness (A Scale) of not more than 96 according to JIS-K6301 wherein said thermoplastic elastomer composition has a bending modulus according to JIS-K7203 of 0 to 1,000 kg/cm².

11. A thermoplastic elastomer composition according to claim 10 wherein said component (B) is a thermoplastic polyester elastomer which is an elastomer obtained by polycondensation of an aliphatic and/or alicyclic diol having 2 to 12 carbon atoms, an aromatic dicarboxylic acid or an alkyl ester thereof, and a polyalkylene ether glycol.

* * * * *